

RABAH ALI KHALIL

A Simple Approach to

Quantum Chemistry

CHEMISTRY RESEARCH AND APPLICATIONS

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A SIMPLE APPROACH TO QUANTUM CHEMISTRY

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In Memory of my Father and Mother

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PREFACE

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Remarkable improvements in the applications of quantum mechanical calculations for developing and understanding essential issues in different aspects are necessary. These are including medicinal, pharmaceutical, renewable energies, and some others. Moreover, this will be the probable success in developing what the so-called “quantum computer” encourages people in order to know about the subject of quantum mechanics. Therefore, an adopted book for simply introducing the principle of quantum mechanics seems to be interesting. The presented book may be considered as a textbook for undergraduate students of the chemistry department as a basic course, and also can be considered as a background for beginners who desire to understand this subject. Indeed, this book may reflect the two decades of experience of

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the author in teaching quantum chemistry to undergraduate students. The presented textbook includes seven chapters, starting from the requested classical mechanics, quantum theory, quantum mechanics, applications of quantum mechanics for some simple systems, approximate methods, atoms, and molecules to the introductory chapter of computational chemistry. As an advanced book in quantum chemistry, many published books have been covered this subject by many respected authors.

Chapter 1

GENERAL INTRODUCTION

1.1. THE DEFINITION OF QUANTUM CHEMISTRY

It seems necessary to define this subject, in order to have a modest idea in this regard. Thus, quantum chemistry may be defined as “a branch of chemistry, concerning the application of quantum mechanics for solving chemical problems, such as the electronic structure of atoms and molecules, and spectroscopy”. This means that the main reason for adopting this field of science is to contribute to solving the accumulated challenges that chemists are facing. The definition needs to explain the term quantum mechanics, which may be defined as “a mathematical system, which has been presented in three different ways with similar results. The first method was adopted by Schrodinger (wave mechanics), the second one was described by Heisenberg (matrix mechanics), and the final method was defined by Dirac (ket & bra mechanics)”.

1.2. COORDINATE SYSTEM

The purpose of using a coordinate system is to describe a point, a curve or a surface in space. There are many different kinds of coordinate systems, such as Cartesian, spherical, and cylindrical. The presented area of quantum chemistry only uses Cartesian and spherical coordinates, as is detailed below.

1.2.1. Cartesian Coordinates

The point (p) can be described through three distances (x , y , and z). In other words, point p is a function of three distances (x , y , and z), as shown clearly in Figure 1-1.

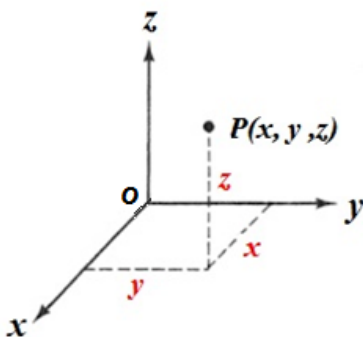


Figure 1-1. The presentation of a three-dimensional Cartesian coordinate system, with origin O and axis lines x , y , and z , is oriented as shown by the arrows. The black dot shows the point with coordinates $x = 2$, $y = 3$, and $z = 4$.

1.2.2. Spherical Coordinates

The point (p) can be described through one distance (the radial r) and two angles (θ and ϕ), as exhibited in Figure 1-2.

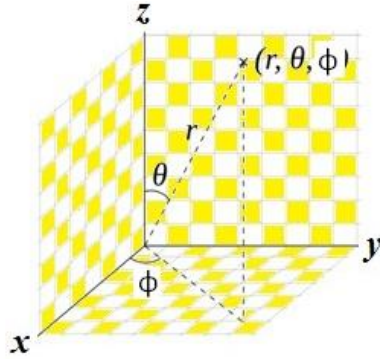


Figure 1-2. The spherical coordinates (r , θ , and ϕ), where r is the radial distance, θ (theta) is the polar angle, and ϕ (phi) is the azimuthal angle.

There is a possibility for inverting Cartesian coordinate to spherical and *vice versa*, using the following three equations,

$$x = r \sin \theta \cos \phi \quad (1-1)$$

$$y = r \sin \theta \sin \phi \quad (1-2)$$

$$z = r \cos \theta \quad (1-3)$$

1.3. CONSERVATIVE SYSTEM

A system can be conservative if its total energy remains constant with time. The total energy (E) of the system can be expressed as the sum of both kinetic (T) and potential (U) energies, according to the following equation,

$$E = T + U \quad (1-4)$$

This means that the conservative system is completely isolated with no external effect. In other words, there is no loss in the amount of energy

or momentum through motion, such as the rotation of electrons and the earth around the nucleus and sun, respectively.

1.4. GENERALIZED COORDINATES AND DEGREES OF FREEDOM

The main purpose of dealing with generalized coordinates is to make it convenient for treating systems of multi particles, from a mathematical point of view. Supposedly, there is a conservative system of three particles ($N = 3$), in order to describe the state of this system completely at a given time, one would have to specify the positions and velocities of the three particles. This means we must have 9 positions ($x_1, y_1, z_1; x_2, y_2, z_2; x_3, y_3, \text{ and } z_3$) and 9 velocities ($\dot{x}_1, \dot{y}_1, \dot{z}_1; \dot{x}_2, \dot{y}_2, \dot{z}_2; \dot{x}_3, \dot{y}_3, \text{ and } \dot{z}_3$). Hence, for a system containing N particles, one must have $3N$ positions and $3N$ velocities, which means $6N$ degrees of freedom. Thus, for a system having N particles, there are $3N$ generalized coordinates ($q_i, I = 1, 2, \dots, 3N$), and $3N$ generalized velocities ($\dot{q}_i, I = 1, 2, \dots, 3N$). Similarly, one could express the generalized momentum ($\dot{p}_i$), according to the following formula,

$$p_i = m\dot{q}_i \quad i = 1, 2, \dots, 3N \quad (1-5)$$

where m is the mass of the particle. In general, the use of generalized coordinate makes the mathematical expressions relatively more simple and convenient.

1.5. SPECIALIZED TOPICS IN CLASSICAL MECHANICS

Classical mechanics as formulated by Newton is called Newtonian mechanics, which is not considered as a unique formulation of the

mechanics. This despite the Newtonian mechanics is considered a fairly straightforward approach from a mathematical point of view. However, there are other possible formulations of mechanics. For our purpose, the two common alternative formulations of classical mechanics are the Lagrangian mechanics and Hamiltonian mechanics. The main difference between Newtonian and that of Lagrangian and Hamiltonian mechanics, in addition to mathematical simplicity, is that both of the later mechanics do not require the concept of force as Newtonian, as they are expressed in terms of energy.

1.5.1. Newtonian Mechanics

The Newtonian mechanics can be presented by Newton's second law in dynamics, which gives the required force F for providing an acceleration (a) to the mass (m), as represented by the following famous equation,

$$F = ma \quad (1-6)$$

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

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

where t is time. Thus, Eq. (1-6) can be represented in differential format by the following equation,

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

1.5.2. Lagrangian Mechanics

Appreciated efforts have been made by Lagrange, in order to introduce an alternative to Newtonian mechanics. Sometimes there are practical benefits that arise from the replacement of Newtonian mechanics by Lagrangian mechanics. In other words, in certain situations, the application of Newtonian mechanics is quite tricky, in contrast to that of Lagrangian. The important aspect here is the quantity of the Lagrangian function (L), which defined as the difference between kinetic energy (T) and potential energy (U),

$$L = T - U \quad (1-9)$$

As far as the kinetic energy is a function of velocity v , and the potential energy is a function of position x in one dimension, equation (1-9) can be rewritten as,

$$L_{(x,v)} = T_{(v)} - U_{(x)} \quad (1-10)$$

For a particle that moved in one dimension, the solution by the Lagrangian model will be as follows,

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

Equation (1-11) contains two kinds of derivatives, ordinary (d) and partial (∂). Therefore, we present here some examples of these derivatives, if

$$f(x) = 4x^2 + 3x^6 \quad (1-12)$$

then,

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

This is called an ordinary derivative equation, as it contains only one variable (x). However, if f is a function of two variables (x and y), then, we have to use partial derivatives. For example, if

$$f(x, y) = 3x^3y + 7y^5 + 5x^4y^7 - 8x \quad (1-14)$$

Then, the partial derivatives concerning x and y are,

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

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

1.5.2.1. Example: Simple Harmonic Oscillator

Figure 1-3 is the schematic presentation of the simple harmonic oscillator of mass m , and x is the distance from the equilibrium position.

According to Hooke's law,

$$F = -kx \quad (1-17)$$

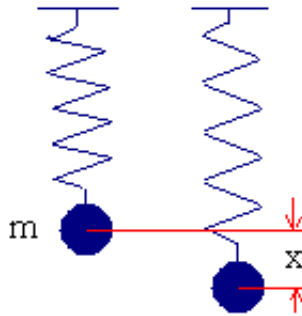


Figure 1-3. Simple harmonic oscillator.

where x is the measured distance from the equilibrium position, and k is the force constant. The minus sign is presented in this equation because the force is in the opposite direction. On the other hand, the force of this kind of motion may also be presented as the negative gradient of the potential energy U :

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

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

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

Then, the potential energy of this system could be obtained by taking the integral of the latter equation,

$$\int_0^\infty \partial U = k \int_0^\infty x \partial x \quad (1-20)$$

which gives:

$$U = \frac{1}{2} kx^2 \quad (1-21)$$

The kinetic energy T of the simple harmonic oscillator can be represented by,

$$T = \frac{1}{2} mv^2 \quad (1-22)$$

where m is the mass of a particle and v is the velocity. Thus, the Lagrangian function $\{L = T - U \text{ (1-9)}\}$ can be rewritten as:

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

Since the present example is in one dimension, Lagrangian equation in one dimension $\{\frac{d}{dt}(\frac{\partial L}{\partial v}) - \frac{\partial L}{\partial x} = 0$ (1-11)} can substitute L of Eq. (1-23) as follows:

$$\frac{d}{dt} \left[\frac{\partial}{\partial v} \left(\frac{1}{2} m v^2 - \frac{1}{2} k x^2 \right) \right] - \frac{\partial}{\partial x} \left(\frac{1}{2} m v^2 - \frac{1}{2} k x^2 \right) = 0 \quad (1-24)$$

Evaluating the partial derivatives, one could obtain,

$$\frac{d}{dt} (m v) + k x = 0 \quad (1-25)$$

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

$$m \frac{d^2 x}{dt^2} + k x = 0 \quad (1-26)$$

According to Eq. (1-7), the acceleration (a) is equal to $\frac{d^2 x}{dt^2}$, and Eq. (1-26) can be represented as,

$$m a + k x = 0 \quad (1-27)$$

Interestingly, Eq. (1-27) represents both Newton's second law ($F = ma$) and Hooke's law ($F = -kx$), supporting the correctness of Lagrangian function and equation.

1.5.3. Hamiltonian Mechanics

Hamiltonian mechanics depends merely on that of Lagrangian through the quantity of Hamiltonian function H , which contains Lagrangian function L . However, Lagrangian Eq. (1-11) expresses the motion of a particle, as a single-order differential equation. Nevertheless

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

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

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

On the other hand, the Hamiltonian function H is a quantity, which is defined by the following mathematical expression,

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

where H is the Hamiltonian function, p_i is the generalized momentum, $\dot{q}_i$ is the generalized velocities, and L is the Lagrangian function.

1.5.3.1. Example: Simple Harmonic Oscillator (Hamiltonian Function)

According to Eq. (1-30), one needs to find the kinetic and potential energies in order to substitute the Lagrangian function (Eq. 1-23). These energies were already defined in Eqs. (1-21) and (1-22), as $U = \frac{1}{2}kx^2$ and $T = \frac{1}{2}mv^2$. On the other hand, the momentum p can be expressed by,

$$p = mv \quad (1-31)$$

Thus, for $N = 1$ and through substituting Eqs. (1-23) and (1-31), into Eq. (1-30), one can get,

$$H = mv^2 - (\frac{1}{2}mv^2 - \frac{1}{2}kx^2) \quad (1-32)$$

then,

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

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

$$H = T + U \quad (1-34)$$

This means Hamiltonian functions are defined as the sum of kinetic and potential energies similar to the total energy of a conservative system. Indeed, this equation is considered one of the most important equations in quantum chemistry.

1.5.3.2. Example: Simple Harmonic Oscillator (Hamiltonian

Equation, $\frac{dp}{dt} = -\frac{\partial H}{\partial x}$)

Substituting the Hamiltonian function (1-33) in Eq. (1-29) gives,

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

Taking the partial derivatives, one can get,

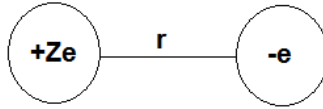
$$\frac{dp}{dt} = -kx \quad (1-36)$$

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

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

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

1.5.3.3. Example: Write the Hamiltonian Function for a Hydrogen Atom



The atomic number (Z) of the H atom is equal to one. Supposedly, the nucleus is fixed and the electron moves around it, therefore, the kinetic energy of the nucleus will be equal to zero.

According to Eq. (1-34),

$$H = T + U$$

The kinetic energy of an electron (Eq. (1-22) is,

$$T = \frac{1}{2}mv^2$$

In order to make the kinetic energy described by momentum, instead of velocity, the right side of the Eq. (1-22) will be multiplied by $\frac{m}{m}$, which does not disturb the equation, one can get,

$$T = \frac{1}{2}mv^2 \times \frac{m}{m} = \frac{m^2v^2}{2m} \quad (1-38)$$

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

$$T = \frac{p^2}{2m} \quad (1-39)$$

The potential energy for two charged particles is described by the interaction between those charges, and the distance r between them,

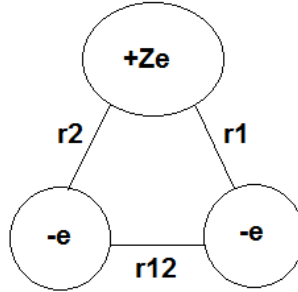
$$U = \frac{(+Ze)(-e)}{(4\pi\epsilon_0)r} = \frac{-e^2}{4\pi\epsilon_0 r} \quad (1-40)$$

where $4\pi\epsilon_0$ is the Coulombs constant, as $\epsilon_0 = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$, Thus, the Hamiltonian function for H atom is,

$$H = \frac{p^2}{2m} + \frac{-e^2}{4\pi\epsilon_0 r} \quad (1-41)$$

1.5.3.4. Example: Write the Hamiltonian Function for a Helium Atom

The atomic number (Z) of *He* atom is equal to two. Supposedly, the nucleus is fixed and the electrons move around it.



$$T = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} \quad (1-42)$$

$$U = \frac{-Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (1-43)$$

$$\therefore H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (1-44)$$

1.6. EXERCISES

1. Write the Hamiltonian function for lithium atom ($Z = 3$).
2. Prove that the Hamiltonian function is equal to the total energy of a conservative system.
3. State two examples of the conservative system.
4. Does the force of Hooke's law have a negative sign?
5. Does the Hamiltonian functions of atoms having more than two electrons are logical? Why?
6. What is the main purpose of generalized coordinates?

Chapter 2

QUANTUM THEORY

2.1. INTRODUCTION

The increase in the number of unresolved problems that scientists were facing in the nineteenth century, led to discovering a modern science, called quantum theory, as was initiated for understanding and treating these problems. The main problems were about the nature of light, electromagnetic energy, atomic and molecular structures. For example, the contradiction between Newton and Huygens about the theory of light is remaining, since the seventeenth century. Indeed, quantum theory was originated in 1900 by Max Planck, through explaining the phenomenon of black body radiation. Therefore, the first hypothesis of this new science was postulated by Planck, containing the word of quanta. Then, considerable support to these hypotheses through some more postulates was given by Einstein, Bohr, Sommerfeld, and de Broglie.

The main concept of quantum theory is that the absorption of electromagnetic energy is not continuous as heat, but discontinuous as a matter. In other words, the energy of the system can take only a certain amount of energy. However, according to classical mechanics, the

energy of the system can be in any quantity and can change by any amount.

2.2. BLACK BODY OR CAVITY RADIATION

Black body radiation is defined as any matter that could emit radiation in all wavelength ranges. Such a state can be obtained by constructing an isolated cavity, as the only energy that can be absorbed is energy in the form of heat, in order to raise the temperature. Thus, the heated cavity will be considered as a black body that emits long ranges of radiation. For example, the heated tungsten metal cannot be considered as a black body, because it only emits radiation at a short-range of wavelengths (visible only). The black body experiment may be explained simply by a box with a small hole that emits a wide range of electronegative radiation, as shown in Figure 2-1.

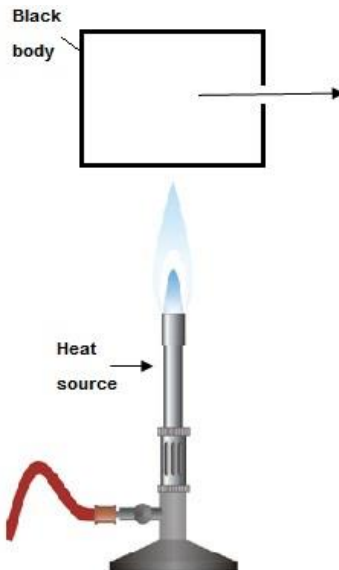


Figure 2-1. The simple scheme explaining the black body radiation.

The type of radiation in Planck's quantization of energy is the heat released from a heated material, called thermal radiation. This experiment was already studied by Rayleigh and Jeans, using classical mechanics. They assumed that the distribution of intensity $I(\nu)$ as a function of frequency (ν), increases with increasing temperature T (Equation 2-1), i.e., a rod of iron appears red at 500°C, and change to bluish at 1000°C.

$$I(\nu) = \frac{8\pi kT}{\lambda^4} \quad (2-1)$$

where k is the Boltzmann constant ($1.38064852 \times 10^{-23} \text{ J K}^{-1}$), T is the absolute or Kelvin temperature, and λ is the radiation wavelength.

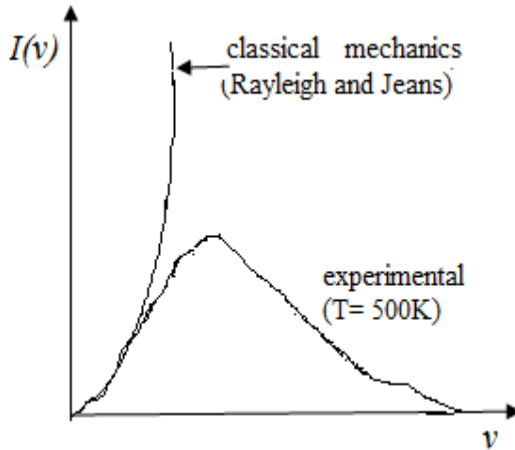


Figure 2-2. The distribution of intensity $I(\nu)$ as a function of frequency ν .

Planck performed an experiment, in order to understand the black body radiation. He surprisingly found that there is a maximum in the relation of $I(\nu)$, as a function of frequency ν (Figure 2-2), which contradicts the assumed model of Rayleigh and Jeans. Such an unexpected result led Planck at the end of 1900 to discover a new science, called quantum theory, and that culminated in his first famous hypothesis

as the first postulate of quantum theory. He postulated that “the energy like matter is discontinuous and consists of large numbers of tiny discrete units of equal portions, called quanta”. The system can only emit or take radiation by quanta of energy (E), which is proportional to the frequency ν ($E = h\nu$), as explained in Figure 2-3. The symbol h is famous or magic Planck constant of the value 6.62607×10^{-34} Js. Thus according to classical mechanics, the system may be able to take any value and to change by any amount of energy. Whereas, by the quantum theory (Planck assumption), a system can have only a unique set of certain values of $h\nu$ or its integer multiplication ($ih\nu, i=1, 2, 3 \dots n$). He developed a model that could cope with the experimental relation of black body radiation, as the following,

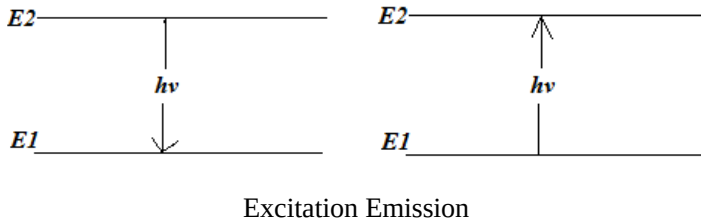


Figure 2-3. The excitation and emission according to the Planck postulate.

$$I(\nu) = \frac{8\pi hC}{\lambda^5} \left(\frac{1}{e^{hC/\lambda kT} - 1} \right) \quad (2-2)$$

where C is the velocity of light. At high frequency, $hC/\lambda kT$ is large enough to make the value of $I(\nu)$ equal to zero. For long wavelength, $hC/\lambda kT \ll 1$, as the relationship will be somewhat similar to that of Rayleigh and Jeans (2-1). An example that may help in understanding the quantization of energy is that not all gas molecules in the atmosphere, absorb the natural light or radiation, as the energy is not enough for excitation, except for those of carbon dioxide and methane gases.

2.3. PHOTOELECTRIC EFFECT

In 1905, Einstein explored the experiment of the photoelectric effect, in order to understand the concept, as Planck did for black body radiation. Figure 2-4 explains the photoelectric effect, using a simple diagram.

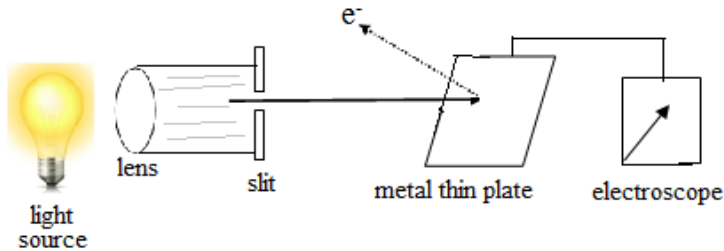


Figure 2-4. The photoelectric effect.

Thus, the incident light at a thin layer plate of metal ejects electrons, which change the charge of a plate from neutral to positive. Einstein supported the 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 has Planck quanta energy ($E = h\nu$)”. Such a particle, then was called photon by Lewis. It should be noted that the photoelectric effect has two more advantages, in addition to the last postulate. It solved the problem of centuries about the nature of light, which behaves as particle-like. The second one is that the photoelectric effect can be considered a source of β -particles or β -ray.

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 ν_0 , which its value depends on the type of metal. On the other hand, the kinetic energy of the ejected electron is proportional to the frequency of incident light. The excess of the kinetic energy of the ejected electron (E_T) can be represented by this equation:

$$E_T = \frac{1}{2}mv^2 = h\nu - h\nu_o = h\nu - W \quad (2-3)$$

where W is the work function of the metal.

2.3.1. Example

What is the maximum velocity of electrons, ejected from Ni metal by a light source of 200 nm wavelength, if the work function of Ni is 5eV? Knowing that the mass of electron is 9.1×10^{-31} kg, the conversion factor is $1\text{eV} = 1.60 \times 10^{-19}$ J, and the velocity of light is $C = 3 \times 10^8 \text{ ms}^{-1}$.

$$\therefore \nu = \frac{C}{\lambda}$$

$$\nu = \frac{3 \times 10^8 \text{ m/s}}{200 \times 10^{-9} \text{ m}} = 1.5 \times 10^{15} \text{ s}^{-1} \text{ or Hz}$$

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

$$E_T = \frac{1}{2}mv^2 \Rightarrow v = \sqrt{\frac{2E_T}{m}} = \sqrt{\frac{2 \times 1.94 \times 10^{-19} \text{ J}}{9.1 \times 10^{-31} \text{ kg}}} = 6.53 \times 10^5 \text{ ms}^{-1}$$

2.3.2. Einstein Mass-Energy Equivalent

Another famous relation that was described by Einstein for the equivalence of mass and energy from the special theory of relativity is:

$$E = mC^2 \quad (2-4)$$

Indeed, this relation is very important in quantum theory, as it will be used in the later postulate of de Broglie.

2.4. BOHR ATOM

In 1911, Rutherford was successfully given a true idea about an atom, which achieved from his experiment of the bombardment of a very thin layer of gold by α -particles. At that time, his new idea has been attacked by electromagnetic theory, stating that the charged particle emits energy by moving.

In 1913, Bohr solved this problem by an interesting combination of classical mechanics with quantum theory. His developed theory may be considered as an addition to the three postulates to quantum theory:

1. There are only certain allowable orbits for an electron in H atom.
2. In these orbits, the magnitude of angular momentum (L) of the electron can only have quantized values, according to the following equation:

$$L = n \left(\frac{h}{2\pi} \right) = n\hbar \quad n = 1, 2, 3, 4, \dots \dots \dots etc \quad (2-5)$$

where n can be considered as the principal orbital quantum number and $\hbar = h/2\pi$.

3. The electron can only pass from one stationary state to another. The frequency of a spectral line (Figure 2-5) due to the transition of that electron, is also quantized and equal to Planck or photon energy,

$$E = E_2 - E_1 = h\nu \quad (2-6)$$

Using the last postulate, one could calculate the wavelength of the transition in the hydrogen atom, by the following model:

$$h\nu = \frac{Z^2 me^4}{8h^2 \epsilon_0^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = 13.6Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] eV \quad (2-7)$$

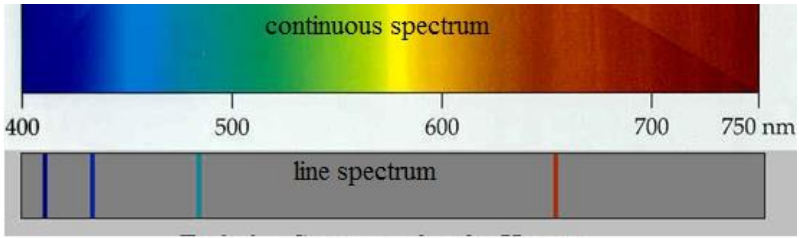


Figure 2-5. The continuous and line spectrum.

Figure 2-6 explains the emission spectrum of the H atom, according to Bohr's assumptions. The energy of each orbital level could be estimated by the following equation,

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

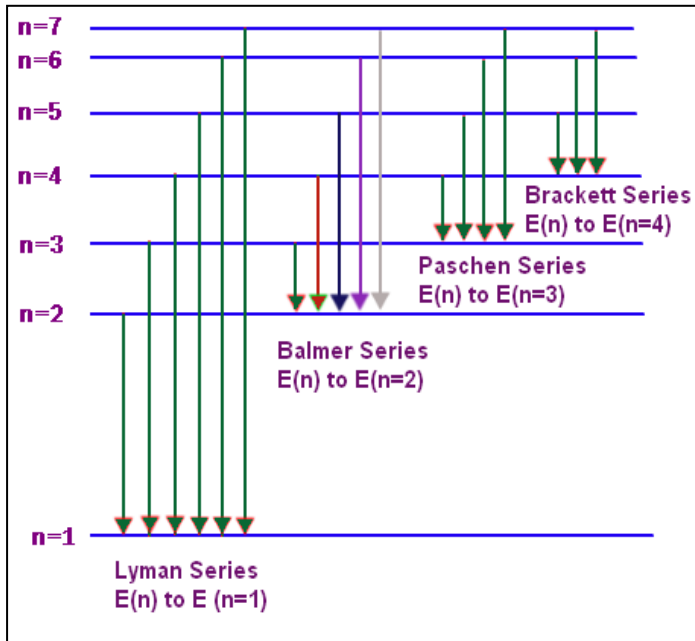


Figure 2-6. The emission spectrum of the H atom.

Despite the remarkable successes of Bohr's theory, it contains two weak points. The first is that the electron moves around the nucleus in cyclic orbits. The second is contradiction with the uncertainty principle, as the momentum and position of an electron can be determined simultaneously with accurate means.

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), $E_n = \frac{13.6 \text{ eV}}{n^2}$

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

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

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

2.5. OLD QUANTUM THEORY (SOMMERFELD QUANTIZATION THEORY)

In 1915, Wilson and Sommerfeld developed a method of quantization, which was applied to several physical systems. 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,

$$\oint p_i dq_i = nh \quad (i = 1, 2, 3, \dots, f) \quad (2-9)$$

where the last integration symbol means the integration of complete cycle, and n is the quantum integer number, $n=0, 1, 2, 3, \dots$ etc. Thus, the real position and momentum of the system, according to the quantum condition must be equal to Planck's constant or its multiplication by an integer number.

2.5.1. Example: Simple Harmonic Oscillator

According to the previous chapter (section 1.5.2.1), the total energy (E) of the simple harmonic oscillator can be represented by the following equation:

$$E = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 \quad (2-10)$$

since $p = mv$, Eq. (2-10) can be rewritten as:

$$E = \frac{p_x^2}{2m} + \frac{kx^2}{2} \quad (2-11)$$

dividing by E with rearrangement gives:

$$\frac{p_x^2}{2mE} + \frac{x^2}{2E/k} = 1 \quad (2-12)$$

The relationship between p_x and x in the last equation can be related to that of an ellipse (Figure 2-7), as introduced by the following:

$$\frac{p_x^2}{b^2} + \frac{x^2}{a^2} = 1 \quad (2-13)$$

where a and b are representing the major and minor semi-axes of the ellipse, respectively, as shown in Figure 2-7. By comparing the equation (2-13) with that of (2-12), one could obtain,

$$a = \sqrt{\frac{2E}{k}} \text{ and } b = \sqrt{2mE} \quad (2-14)$$

The ellipse area is equal to πab , which could also be estimated from a phase diagram that represents the linear motion p_x with x displacement. Thus,

$$\text{Area of ellipse} = \oint p_x dx = \pi ab \quad (2-15)$$

Substituting the values of a and b from Eq. (2-14) in Eq. (2-15), gives:

$$\oint p_x dx = \frac{2\pi E}{\sqrt{k/m}} \quad (2-16)$$

The frequency of oscillation (ω) can be represented by:

$$\omega = \sqrt{k/m} \quad (2-17)$$

by the combination of the last two Eqs. ((2-16) and (2-17)), one could get,

$$\oint p_x dx = \frac{2\pi E}{\omega} \quad (2-17)$$

On the other side, the left side of or integration side of the Sommerfeld quantization rule is parallel to the left side of the last equation. Therefore,

$$\oint p_x dx = nh = \frac{2\pi E}{\omega} \quad (2-18)$$

$$\text{Hence, } E_n = \frac{nh\omega}{2\pi} = n \frac{h}{2\pi} \omega$$

$$\therefore \hbar = \frac{h}{2\pi}$$

$$\therefore E_n = n\hbar\omega \quad (n = 0, 1, 2, 3, 4, \dots) \quad (2-19)$$

The last equation, representing the model for the simple harmonic oscillator is not acceptable, as it contradicts the uncertainty principle. Application of the Sommerfeld quantization to hydrogen atom indicates that the atomic orbits are elliptical (not circle), as it is more realistic in contrast to that of Bohr.

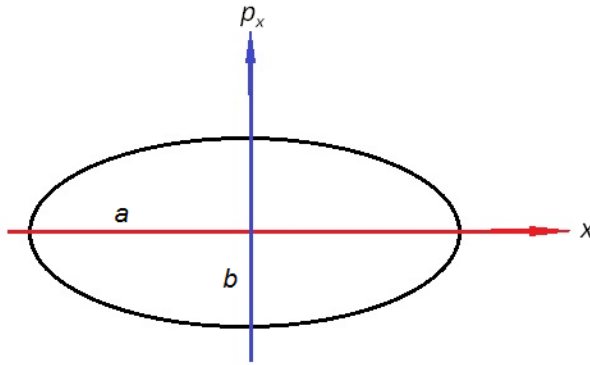


Figure 2-6. The equation of ellipse and phase diagram.

2.6. THE DUAL NATURE OF LIGHT

In 1924, de Broglie stated that the light has dual properties, including particle- and wave-like characteristics. He is postulated that “not only does light display or show particle-like characteristics, but small particles

may at times show wave-like properties”. He derived a very important relationship (Eq. (2-20)) between wavelength and momentum, which is essential for quantum mechanics,

$$p = \frac{h}{\lambda} \quad (2-20)$$

The derivation of this model was as follows,

The energy of a photon is $E = h\nu$, at the same time the mass-energy equivalence (Eq. (2-4)) is $E = mC^2$; therefore,

$$h\nu = mC^2, \nu = \frac{c}{\lambda}$$

Then,

$$\frac{hc}{\lambda} = mC^2 \Rightarrow \frac{h}{\lambda} = mC,$$

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

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

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

2.7. EXERCISES

1. Does Planck's constant play an important role in the quantum theory? Why? Where Planck's constant is coming from?
2. Which type of energy Planck derived his postulate of quantum theory from?

3. All air gases of the atmosphere could absorb natural radiation. Why?
4. What is the maximum velocity of electrons ejected from material by 80-nm photons, are they bound to the material by 4.73 eV?
5. What is the relationship between the frequency of light and the speed of ejected electrons?
6. Is it true that all photons have the same energy?
7. Einstein mass-energy equivalent is a very important equation for quantum theory and also for quantum mechanics. Discuss why?
8. State the differences between line- and continuous-spectrums.
9. What is the main problem of quantum theory?

Chapter 3

QUANTUM MECHANICS

3.1. INTRODUCTION

Despite the unlimited efforts that introduced throughout quantum theory with several remarkable successes, a weak point that worked as a defect in such a valuable science is the contradiction with the uncertainty principle. However, quantum theory can be considered as the skeleton of quantum mechanics. In 1926, Schrödinger made a shortcut to this problem by deriving his famous wave equation that considered as a breakthrough to new science, called quantum mechanics. After the presentation of Schrödinger about wave mechanics, this science was mathematically represented by another two scientists; one by Heisenberg, called matrix mechanics, and the other by Dirac, which called ket & bra mechanics. In this book, we will concern about the Schrödinger mechanics, representing the system by a wave.

There are two important definitions (dynamical variable and observable), which should be considered for understanding throughout the following postulates. The dynamical variable is any property of a system such as position, energy, momentum, and so on. Observable is any dynamical variable, which can be measured.

3.2. POSTULATES OF QUANTUM MECHANICS

Any new science should be buildup by several postulates, as we previously have seen in the last chapter. However, the number and contents of the postulates of quantum mechanics depend on the scientist, dealing with this subject. Here, we will take only five postulates as follows:

Postulate I

The state of a dynamical system of N particles is fully specified by an acceptable wave function $\Psi(q, t)$, which depends on the coordinates and time. The important quantity $\Psi^*(q, t) \Psi(q, t) d\tau$ is the probability that the particle lies in the volume element $d\tau$, located at q at time t , which can be expressed by the following formula:

$$\int \Psi^*(q, t) \Psi(q, t) d\tau = 1 \quad (3-1)$$

The volume element symbol $d\tau$ denotes the three-dimensional aspect of all space integration, which can be expressed as follows:

$$\iiint \Psi^*(q, t) \Psi(q, t) dx dy dz = 1 \quad (3-2)$$

Any function can be considered acceptable if it meets the following three requirements:

1. It must be continuous.
2. It must have one value.
3. Its square integral of the function must have a finite value (neither zero nor infinity).

$$\int |\varphi(x)|^2 dx \neq 0 \text{ or } \infty \quad (3-3)$$

The symbol $*$ on the psi (Ψ^*), indicates the presence of a complex number, containing square roots of -1 ($\sqrt{-1}$ or i). Let us assume that C is a complex number, which can be expressed by the following model:

$$C = A + iB \quad (3-4)$$

where A and B are real numbers. The complex conjugate of C is written as C^* , which is formed by replacing i , wherever it appears by $-i$. Thus,

$$C^* = A - iB \quad (3-5)$$

The magnitude or absolute value of a complex number is defined as:

$$|C| = \sqrt{CC^*} = \sqrt{A^2 + B^2} \quad (3-6)$$

Postulate II

For every observable in classical mechanics, there is a corresponding linear Hermitian operator in quantum mechanics. Two steps needed to evaluate the Hermitian operator for any observable quantity. Firstly, by writing the classical expression for the observable, then, replacing the momentum p_q by the following differential operator:

$$\frac{\hbar}{i} \left(\frac{\partial}{\partial q} \right) \quad (3-7)$$

where i is $\sqrt{-1}$. Indeed, postulate II could be considered as a bridge between classical and quantum mechanics. Furthermore, if the observable does not have momentum (velocity must be changed to

momentum), such as potential energy. The Hermitian operator will be the same as the classical expression. Thus, the quantum mechanical operator of the kinetic energy of one-dimensional problem can be evaluated as follows:

$$T = \frac{p_x^2}{2m} \quad (3-7)$$

According to postulate II, the momentum will be replaced by the differential expression (Eq. (3-7)):

$$\hat{T} = \frac{1}{2m} \left[\left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \right] \quad (3-8)$$

$$\therefore \hat{T} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (3-9)$$

Whereas, the kinetic energy for the three-dimensional quantum mechanical operator can be estimated as follows:

$$T = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \quad (3-10)$$

$$\hat{T} = \frac{1}{2m} \left[\left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) + \left(\frac{\hbar}{i} \frac{\partial}{\partial y} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial y} \right) + \left(\frac{\hbar}{i} \frac{\partial}{\partial z} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial z} \right) \right] \quad (3-11)$$

$$\hat{T} = \frac{-\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad (3-12)$$

The differential part between the brackets in the last equation is equal to the Laplacian operator in Cartesian coordinate, which has the symbol of ∇^2 as shown below:

$$\nabla^2 = \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad (3-13)$$

$$\therefore \hat{T} = \frac{-\hbar^2}{2m} \nabla^2 \quad (3-14)$$

Thus, the Hamiltonian operator $\hat{H}$ for the electron can be evaluated by the following formula:

$$H = T + U$$

$$H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + U \quad (3-15)$$

$$\hat{H} = \frac{1}{2m} \left[\left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial x} \right) + \left(\frac{\hbar}{i} \frac{\partial}{\partial y} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial y} \right) + \left(\frac{\hbar}{i} \frac{\partial}{\partial z} \right) \left(\frac{\hbar}{i} \frac{\partial}{\partial z} \right) \right] + \hat{U} \quad (3-16)$$

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + \hat{U} \quad (3-17)$$

Accordingly, the Hamiltonian operator for the one-dimensional movement of an electron can be presented by the following equation:

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{U} \quad (3-18)$$

Postulate III

In any measurement of the observable that associated with $\hat{A}$ operator, the magnitude of a_i value must be satisfied with the following eigenvalue equation,

$$\hat{A}\Psi_i = a_i\Psi_i \quad (3-19)$$

where $\hat{A}$ is the quantum mechanics operator, Ψ_i is the wave function, which also called eigenfunction, and a_i is the eigenvalue. Thus, such type of equation called the eigenvalue equation as in the following example:

$$\frac{d}{dx} (e^{3x}) = 3e^{3x}$$

However, postulate III represents the Schrödinger equation (3-20), which will be derived later,

$$\hat{H}\Psi = E\Psi \quad (3-20)$$

where E is the total energy of a conservative system.

Postulate IV

The average or expectation value of the observable a , corresponding to the operator $\hat{A}$ can be measured by this equation:

$$a = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau} \quad (3-21)$$

If the function Ψ is normalized (Eq. (3-22)), the Eq. of expectation value (3-21) will be changed to Eq. (3-23).

$$\int \Psi^* \Psi d\tau = 1 \quad (3-22)$$

$$a = \int \Psi^* \hat{A} \Psi d\tau \quad (3-23)$$

The equation of postulate IV can be proved as follows. According to postulate III (3-19),

$$\hat{A}\Psi = a\Psi \times \Psi^*$$

multiplication of both sides of Eq. (3-19) by Ψ^* does not disturb the equation, therefore,

$$\Psi^* \hat{A} \Psi = \Psi^* a \Psi$$

Taking the integral of this equation, one could get,

$$\int \Psi^* \hat{A} \Psi d\tau = a \int \Psi^* \Psi d\tau$$

$$\therefore a = \frac{\int \Psi^* \hat{A} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

Postulate V

The wave function Ψ is the state function of a system that changes by time, according to the time-dependent Schrödinger equation.

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (3-24)$$

Our systems such as atoms and molecules are conservatives, so no need for using the time-dependent Schrödinger equation of this postulate. This postulate is mostly used by scientists, who are dealing with quantum physics.

3.3. SCHRÖDINGER WAVE EQUATION

As Schrödinger describes the system by a wave, his famous equation can be derived from the simplest case of wave (string vibration). One could imagine the vibrating string, by fixing a thread to a wall nail and pulled carefully by hand, then hit the end of the thread by finger. A clear

wave will be appeared and transferred to the nail, representing the string vibration as explained in Figure 3-1.

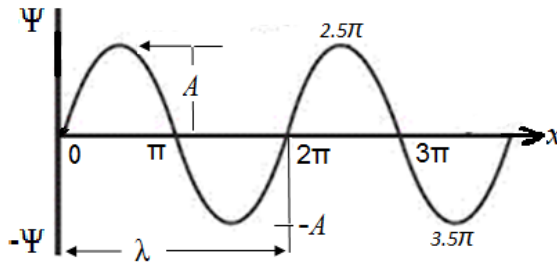


Figure 3-1. A sine wave of string vibration.

Figure 3-1 shows a sine wave; the value of psi (Ψ) is a function of the position x , as described by the following model:

$$\Psi = A \sin bx \quad (3-25)$$

where A is the maximum value of Ψ , and b is a constant that depends on the wave in question. The later unknown constant can be expressed in terms of the wavelength of the wave. According to Figure 3-1, at the point of origin, Ψ is equal to zero, as x and A are both equal to zero, concerning Eq. (3-25). The function Ψ will attain its maximum value at maximum A and $bx = \pi/2$. At π point, Ψ will be also zero as A and $\sin \pi$ both will be zero. Then, Ψ will reach its minimum value at the lowest A and $bx = 3\pi/2$. When $bx = 2\pi$, one could see that at this point $x = \lambda$, therefore $b\lambda = 2\pi$, and then one could substitute the unknown b constant in terms of the wavelength, following this formula:

$$b = \frac{2\pi}{\lambda} \quad (3-26)$$

Substituting b in Eq. (3-26) in the original Eq. (3-25) makes the sine wave in terms of wavelength, as follows:

$$\Psi = A \sin \frac{2\pi x}{\lambda} \quad (3-27)$$

Similarly, a cosine wave also can be described by this equation:

$$\Psi = B \cos \frac{2\pi x}{\lambda} \quad (3-28)$$

The more general wave description of Ψ can be achieved simply by the sum of the above sine and cosine expressions.

$$\Psi = A \sin \frac{2\pi x}{\lambda} + B \cos \frac{2\pi x}{\lambda} \quad (3-29)$$

The wavelength in this equation can be replaced in terms of momentum, according to the de Broglie model ($\lambda = h/p$), as follows:

$$\Psi = A \sin \frac{2\pi p x}{h} + B \cos \frac{2\pi p x}{h} \quad (3-30)$$

On the other side, the Hamiltonian function of an electron can be represented by these equations:

$$H = E = T + U \quad (3-31)$$

$$H = E = \frac{p^2}{2m} + U \quad (3-32)$$

$$\frac{p^2}{2m} = E - U \times \Psi \quad (3-33)$$

$$\frac{p^2}{2m} \Psi = (E - U)\Psi \quad (3-34)$$

If one differentiates Ψ in Eq. (3-30) twice concerning x , one could obtain the following:

$$\frac{\partial \Psi}{\partial x} = \frac{2\pi p}{h} \left[A \cos \frac{2\pi p x}{h} - B \sin \frac{2\pi p x}{h} \right] \quad (3-35)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{4\pi^2 p^2}{h^2} \left[-A \sin \frac{2\pi p x}{h} - B \cos \frac{2\pi p x}{h} \right] \quad (3-36)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{-4\pi^2 p^2}{h^2} \left[A \sin \frac{2\pi p x}{h} + B \cos \frac{2\pi p x}{h} \right] \quad (3-37)$$

The functions inside the brackets in the last Eq. are simply equal to Ψ , according to Eq. (3-29). Therefore,

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{-4\pi^2 p^2}{h^2} \Psi \quad (3-38)$$

multiplying both sides of Eq. (3-37) by $h^2/4\pi^2$ gives:

$$p^2 \Psi = \frac{-h^2}{4\pi^2} \frac{\partial^2 \Psi}{\partial x^2} \quad (3-39)$$

dividing both sides of Eq. (3-37) by $2m$, one could get:

$$\frac{p^2 \Psi}{2m} = \frac{-h^2}{8\pi^2 m} \frac{\partial^2 \Psi}{\partial x^2} \quad (3-40)$$

substituting Eq. (3-40) for $p^2 \Psi/2m$ in Eq. (3-34), one could get:

$$\frac{-h^2}{8\pi^2 m} \frac{\partial^2 \Psi}{\partial x^2} = (E - U) \Psi \quad (3-41)$$

$$\frac{-h^2}{8\pi^2 m} \frac{\partial^2 \Psi}{\partial x^2} + U \Psi = E \Psi \quad (3-42)$$

$$\left[\frac{-h^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} + U \right] \Psi = E \Psi \quad (3-43)$$

According to Eq. (3-18), the functions within the brackets are equal to the Hamiltonian operator, where $\hat{U} = U$, as there is no momentum in this function. Thus, Eq. (3-34) can be represented as the Schrödinger equation (3-20):

$$\hat{H}\Psi = E\Psi$$

Noting that the last equation is derived for the one-dimensional system, but it can be extended to three-dimensional problems just by using the three-dimensional expression of the Hamiltonian operator (3-17), like the following:

$$\hat{H} = \frac{-\hbar^2}{2m} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] + \hat{U} \quad (3-44)$$

However at the same time, there is no change in the terms of the Schrödinger wave equation whether for one or three-dimensional systems, and it remains as follows:

$$\hat{H}\Psi = E\Psi$$

It should be noted that the wave function ψ (Ψ) is a function of position, but at the same time does not reflect the probability of finding a particle at somewhere in space. This is because the value of any probability must lie between one and zero, as clearly shown by Figure (3-1) that Ψ could take a negative sign that contradicts the principle of probability. Therefore, the square of Ψ (Ψ^2) could give the probability of finding the position of the particle. If Ψ is a complex function, the absolute square ($\Psi^*\Psi$) is used instead of Ψ^2 .

3.4. HERMITIAN OPERATOR

Any operator that could satisfy the following integrated relation can be considered as a Hermitian operator. In other words, A Hermitian operator can be described by the following equation:

$$\int \Psi_i^* \hat{A} \Psi_j d\tau = \int \Psi_j \hat{A}^* \Psi_i^* d\tau \quad (3-45)$$

All operators in quantum mechanics are Hermitian. On the other hand, the eigenvalues of a Hermitian operator must always be real, to prove that one could do the following:

According to postulate III (3-19),

$$\hat{A} \Psi_i = a_i \Psi_i$$

The complex conjugate of this relation (3-19) is:

$$\hat{A}^* \Psi_i^* = a_i^* \Psi_i^* \quad (3-46)$$

Multiplying Eq. (3-19) by Ψ_i^* and Eq. (3-46) by one Ψ_i , the following two relations can be achieved. Noting that the order of multiplication of the operator is relevant ($\hat{A} \Psi_i \neq \Psi_i \hat{A}$),

$$\Psi_i^* \hat{A} \Psi_i = \Psi_i^* a_i \Psi_i \quad (3-47)$$

$$\Psi_i \hat{A}^* \Psi_i^* = \Psi_i a_i^* \Psi_i^* \quad (3-48)$$

by taking the integral of Eqs. (3-47) and (3-48), one could obtain,

$$\int \Psi_i^* \hat{A} \Psi_i d\tau = \int \Psi_i^* a_i \Psi_i d\tau = a_i \int \Psi_i^* \Psi_i d\tau \quad (3-49)$$

$$\int \Psi_i \hat{A}^* \Psi_i^* d\tau = \int \Psi_i a_i^* \Psi_i^* d\tau = a_i^* \int \Psi_i \Psi_i^* d\tau \quad (3-50)$$

Since $\hat{A}$ was postulated as a Hermitian, the left sides of Eqs. (3-49) and (3-50) must be equal, according to the Hermitian operator (Eq. (3-45)):

$$\int \Psi^* \hat{A} \Psi d\tau = \int \Psi \hat{A}^* \Psi^* d\tau$$

Therefore,

$$a_i \int \Psi_i^* \Psi_i d\tau = a_i^* \int \Psi_i \Psi_i^* d\tau \quad (3-51)$$

Since Ψ_i and Ψ_i^* are both functions (not operators), the order of multiplication is immaterial,

$$\int \Psi_i^* \Psi_i d\tau = \int \Psi_i \Psi_i^* d\tau \quad (3-52)$$

therefore,

$$a_i = a_i^* \quad (3-53)$$

Thus, the eigenvalue of the Hermitian operator must be real, as only the real numbers are equal to their complex conjugates.

3.5. NORMALIZATION AND ORTHOGONALITY

If one supposes that there is an electron moving in the x -axis, the probability of finding the electron within the region between x and $x+dx$ is given by $\Psi^2 dx$, according to postulate I, while the total probability of finding the electron in the x -axis can be given by the integral of this quantity (Eq. (3-54)):

$$\int_{-\infty}^{\infty} \Psi^2 dx \text{ or } \int_{-\infty}^{\infty} \Psi \Psi dx \quad (3-54)$$

The value of this integral describes the probability of finding the electron in the x -axis, which stretches from $-\infty$ to ∞ . This must be equal to unity, as supposedly, there is an existing electron there. Hence,

$$\int_{-\infty}^{\infty} \Psi \Psi dx = 1 \quad (3-55)$$

this is for a one-dimensional problem. Similarly, for three-dimensional system $\Psi^2 dx dy dz$ can be presented by:

$$\iiint_{-\infty}^{\infty} \Psi \Psi dx dy dz = 1 \quad (3-56)$$

which may be rewritten as follows:

$$\int \Psi \Psi d\tau = 1 \quad (3-57)$$

The last important equation is called the normalization requirement. When and where does anyone deal with normalized Ψ , this criteria must be satisfied.

On the other side, if the function Ψ is not normalized, it can be converted to be normalized, by multiplying by a constant that called normalization constant. For example, write the normalization constant for the function Ψ , according to the following integral equation:

$$\int \Psi \Psi d\tau = k \quad (3-58)$$

The solution to this problem can be evaluated as follows. Suppose the function Ψ is normalized by multiplying by N constant, thus, Eq. (3-58) can be represented as:

$$\int (N\Psi)(N\Psi) d\tau = 1 \quad (3-59)$$

then,

$$N^2 \int \Psi \Psi d\tau = 1 \quad (3-60)$$

The expression within an integral part of the above equation (3-60) is equal to k , according to Eq. (3-58) that belongs to the problem itself. Thus, substituting Eq. (3-58) to Eq. (3-60) will give:

$$N^2 k = 1 \quad (3-61)$$

$$\therefore N = \sqrt{\frac{1}{k}} \quad (3-62)$$

Thus, the normalization constant can be evaluated according to the above example.

Another interesting property of wave function Ψ is its orthogonality. In order to understand the orthogonality term, consider there are two orbitals, and their wave functions Ψ_A and Ψ_B . For example, the atomic orbitals of $1s$ and $2s$ exist for a hydrogen atom. These functions (Ψ_A and Ψ_B) can be orthogonal if the integral of their product is equal to zero as follows:

$$\int \Psi_A \Psi_B d\tau = 0 \quad (3-63)$$

On the other side, the value that resulted from the integral of these functions (Eq. (3-64)) can be considered a measure of the overlap between the orbitals A and B , as the larger the value of the integral is, the greater the degree of overlap will be.

$$\int \Psi_A \Psi_B d\tau = \text{where } A \neq B \quad (3-64)$$

The requirement that the integral is equal to zero (Eq. (3-64)), indicating that these two wave functions are orthogonal as imply that Ψ_A and Ψ_B have no overlap between their orbitals.

To prove that the resulted value from the integral of orthogonalized functions is equal to zero, let us discuss the two Schrödinger equations for the two orbitals A and B ;

$$\hat{H}\Psi_A = E_A\Psi_A \quad (3-65)$$

$$\hat{H}\Psi_B = E_B\Psi_B \quad (3-66)$$

where E_A and E_B are the energies of electrons in the orbitals A and B , respectively ($1s$ and $2s$ orbitals are the examples). Multiplying Eq. (3-65) by Ψ_B and Eq. (3-66) by Ψ_A , one can get:

$$\Psi_B\hat{H}\Psi_A = \Psi_BE_A\Psi_A \quad (3-67)$$

$$\Psi_A\hat{H}\Psi_B = \Psi_AE_B\Psi_B \quad (3-68)$$

The integral of all functions in both Eqs. (3-67) and (3-68) leads to:

$$\int \Psi_B\hat{H}\Psi_A d\tau = E_A \int \Psi_B\Psi_A d\tau \quad (3-69)$$

$$\int \Psi_A\hat{H}\Psi_B d\tau = E_B \int \Psi_A\Psi_B d\tau \quad (3-70)$$

Since E_A and E_B are the numbers, it is permissible to eliminate them from the integral expression. According to the Hermitian operator:

$$\int \Psi_B\hat{H}\Psi_A d\tau = \int \Psi_A\hat{H}\Psi_B d\tau \quad (3-71)$$

also, Ψ_A and Ψ_B both are functions, therefore,

$$\int \Psi_A \Psi_B d\tau = \int \Psi_B \Psi_A d\tau \quad (3-72)$$

Subtracting Eq. (3-70) from Eq. (3-69) gives:

$$0 = E_A \int \Psi_B \Psi_A d\tau - E_B \int \Psi_A \Psi_B d\tau \quad (3-73)$$

$$0 = (E_A - E_B) \int \Psi_A \Psi_B d\tau \quad (3-74)$$

Since $E_A \neq E_B$, therefore, in order to satisfy Eq. (3-74), the integral expression must be equal to zero. Thus,

$$\int \Psi_A \Psi_B d\tau = 0$$

Noting that the above assumption of E_A not equal to E_B is not imperative. It may be shown in the last integral *equation* $\int \Psi_A \Psi_B d\tau = 0$, even in the case of $E_A = E_B$. If E_A does equal to E_B , then Ψ_A and Ψ_B are said to be degenerate. In other words, when two eigenfunctions are corresponding to the same eigenvalue, they can be considered as degenerate. For example, two or more orbitals have the same energy, such as p orbitals; p_x , p_y , and p_z . The latter phenomenon is usually called degeneracy.

3.6. ORTHONORMALITY (ORTHONORMAL FUNCTIONS)

If the wave functions are orthogonal to each other and individually normalized, they will be called orthonormal functions. Mathematically, orthonormal functions can be summarized as follows:

$$\int \Psi_n \Psi_m d\tau = \begin{bmatrix} 0 & n \neq m \\ 1 & n = m \end{bmatrix} = \delta_{n,m} \quad (3-75)$$

The quantity $\delta_{n,m}$ is called kronecker delta function, which has only two values as follows:

$$\begin{aligned}\delta_{n,m} &= 0 & \text{if } n \neq m \\ \delta_{n,m} &= 1 & \text{if } n = m\end{aligned}$$

3.7. UNCERTAINTY PRINCIPLE

In the 1920s, considerable concern about the accuracy of measurements was investigated by Bohr and Heisenberg. They thought about hypothetical experiments, adopted in order to establish how precisely the behavior of subatomic particles could be estimated. The two variables, which could determine this behavior are both the position and momentum of the particle. 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 reached that there must always be uncertainties in measurement in such a way that the product of uncertainty in position, Δx , and in momentum, Δp , is

$$\Delta x. \Delta p \geq \hbar \quad (3-76)$$

The importance of this expression is attributed to the uncertainty principle or sometimes Heisenberg uncertainty principle, which can be stated as follows: the position and momentum cannot both be determined in an accurate way simultaneously. However, the uncertainty principle is not limited to position and speed or momentum, the same manner for time and energy, as the following:

$$\Delta E. \Delta t \geq \hbar \quad (3-77)$$

In contrast to classical mechanics, the uncertainty principle has an essential aspect, when one deals with a system that has identical particles such as atoms and molecules. This is due to that any distinguishing between identical particles such as electrons are considered to be a remarkable mistake, which must be forbidden. Such a mistake may arise, as in some cases the uncertainty in the measurements of these particles is larger than the difference between the behaviors of those particles. The concept of avoiding the distinguishability between identical particles, it significantly increases the complexity in solving the problems of atoms and molecules.

3.8. EXERCISES

1. Write the normalization constant for the function Ψ , according to the following integral formula $\int \Psi^* \Psi d\tau = 5$.
2. Prove that the eigenvalue of the Hermitian operator is always real.
3. Prove that the integral of orthogonality ($\int \phi_A \phi_B d\tau$) is equal to zero.
4. Write the Hamiltonian operator for a helium atom.
5. Postulate II can be considered as a bridge between classical and quantum mechanics. Why?
6. What are the conditions of an acceptable function?
7. Why the time-dependent Schrödinger equation (postulate V) must not contain the energy term E ?
8. What is the relation between the dynamical variable and observable?

Chapter 4

APPLICATIONS OF QUANTUM MECHANICS FOR SOME SIMPLE SYSTEMS

4.1. INTRODUCTION

AS it was mentioned at the beginning of this book, several problems require a proper new science to be solved. In general, there are three main steps for solving the problems, using quantum mechanics (Schrödinger equation):

1. Write the Hamiltonian's function of the system, according to classical mechanics.
2. Evaluate the Hamiltonian operator from its corresponding function, using postulate II.
3. Substitute the Hamiltonian operator into the Schrödinger equation and solve the resulted differential equation, in order to obtain the energy of the system, as well as the corresponding wave function for getting information about the positions.

4.2. PARTICLE IN A BOX

The main reason for taking this hypothetical example is to have an idea about the movement of electrons within molecules, and also this example could provide a complete demonstration regarding the solution of problems, using the Schrödinger equation or quantum mechanics.

Imagine a particle with mass (m) constrained to move within the x -axis in a box of length L . This may be done if one assumes that the potential energy of the particle is zero when it is inside the box, and infinite outside the box (Figure 4-1). Hence, it is impossible for a particle with zero potential energy to be outside or at the boundaries of the box, due to the existing infinite potential energy. Therefore, the particle can never leave the box, just moves horizontally between the two sides of the box.

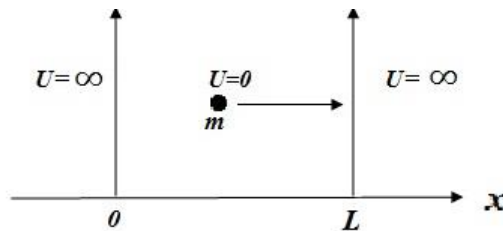


Figure 4-1. A particle in a box of length L .

Since Ψ^2 is the probability of finding the particle at any point, and since the particle cannot leave the box, Ψ^2 must be equal to zero at the boundaries and everywhere outside the box. Therefore, Ψ is also equal to zero (the square root of zero is zero) at the boundaries, and everywhere outside the box, which can be expressed by the following formula:

When x is:

$$\Psi = 0 \quad \left\{ \begin{array}{l} -\infty < x \leq 0 \\ L \leq x < \infty \end{array} \right\} \quad (4-1)$$

It should be noted that the solution of this example will not be usual, using directly the Schrödinger equation. In this special case, the origin of the Schrödinger equation (Eq. (3-30)) will be used as the following:

$$\Psi = A \sin \frac{2\pi px}{h} + B \cos \frac{2\pi px}{h} \quad (3-30)$$

For a particle in a box with potential energy equal to zero ($U=0$), the total energy will be presented as:

$$E = \frac{p^2}{2m} \xrightarrow{\text{then}} p = \sqrt{2mE} \quad (4-2)$$

Substituting the momentum (p) of Eq. (4-2) into Eq. (3-30) gives:

$$\Psi = A \sin \frac{2\pi}{h} \sqrt{2mE} x + B \cos \frac{2\pi}{h} \sqrt{2mE} x \quad (4-3)$$

According to Eq. (4-1), Ψ will be equal to zero when x is equal to zero, substituting $x=0$ into Eq. (4-3), one could get:

$$0 = A \sin 0 + B \cos 0 \quad (4-4)$$

The sine of zero is equal to zero, but the cosine of zero is equal to one. Therefore, in order to satisfy Eq. (4-4), the B constant must be equal to zero ($B=0$). Hence, Eq. (4-3) must be written in this form:

$$\Psi = A \sin \frac{2\pi}{h} \sqrt{2mE} x \quad (4-5)$$

Again, according to Eq. (4-1), Ψ will be equal to zero when x is equal to L , substituting $x = L$ into Eq. (4-5), one could obtain the following equation:

$$0 = A \sin \frac{2\pi}{h} \sqrt{2mE} L \quad (4-6)$$

Thus, Eq. (4-6) can only be satisfied by the following condition:

$$\frac{2\pi}{h} \sqrt{2mE} L = n\pi \quad (n = 1, 2, 3, \dots) \quad (4-7)$$

where n is the quantum number, which is introduced in order to satisfy Eq. (4-6), because only the sine of π , 2π , 3π , and so forth is equal to zero, as explained in Figure 3-1 in the previous chapter. In other words, the scientists dealing with this field do not think or seek about the addition of quantum numbers. The latter comes as a condition for satisfying the Eq. (4-6) in order to be equal to zero. On the other hand, the quantum number n cannot be equal to zero. As clearly seen in Figure 3-1 at 0π , Ψ will be equal to zero, and then Ψ^2 will be equal to zero everywhere, which contradicts the initial assumption of this example, as there is a particle.

According to Eq. (4-7),

$$\text{if } \frac{2\pi}{h} \sqrt{2mE} L = n\pi$$

By dividing both sides of this Eq. by L , one could get:

$$\frac{2\pi}{h} \sqrt{2mE} = \frac{n\pi}{L}$$

The functions expression of the left side of the last Eq. can be substituted with its equivalent in Eq. (4-5), to achieve the wave function model for the particle in a box.

$$\Psi_n = A \sin \frac{n\pi x}{L} \quad (n = 1, 2, 3, \dots) \quad (4-8)$$

On the other hand, the energy levels of the particle in a box can be evaluated as follows. Again, according to Eq. (4-7),

$$\frac{2\pi}{h}\sqrt{2mEL} = n\pi$$

dividing both sides by π gives:

$$\frac{2}{h}\sqrt{2mEL} = n \quad (4-9)$$

$$\therefore E_n = \frac{n^2 h^2}{8mL^2} \quad (n = 1, 2, 3, \dots) \quad (4-10)$$

The possible orbitals for the particle in a box are given by Eq. (4-8) and energies associated with each orbital by Eq. (4-10). Figure 4-2 shows Ψ and Ψ^2 for the lowest three energy levels of a particle in a box, according to Eq. (4-8).

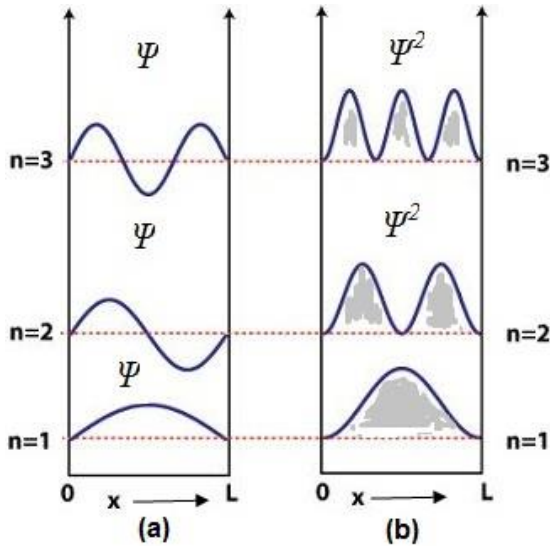


Figure 4-2. (a) Wave function Ψ and (b) probability density function Ψ^2 for the lowest three energy levels of a particle in a box.

Figure (4-2) shows clearly that Ψ cannot give obvious information about the probability of finding the particle in the box, particularly when the energy level exceeds one ($n=2$, $n=3$, and so forth). However, Ψ^2 provides the probability of finding the particle in the areas under the curves with gray color. The observed probability of finding the particle at some points varies with changing the energy levels of the particle. In other words, a particle having energy E_1 is most likely to be found at the center of the box. In contrast, a particle with energy E_2 should never be found in the middle of the box. Moreover, a particle of energy E_3 may have a probability of about 33.3% to be existed at the center of the box.

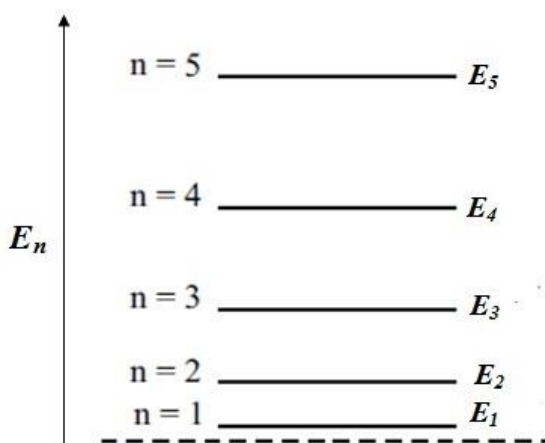


Figure 4-3. The energy levels of the lowest five energies for a particle in a box; the dashed line is zero energy, the energy increases as the square of a quantum number, n .

On the other side, Eq. (4-10) shows that the energy of the particles depends on two variables: n and L . This indicates that the particle mostly will be at $n=1$ level, as it is most stable with the lowest energy. However, increasing the size of the box (L) stabilizes the particle by decreasing its energy. Such a phenomenon may be related to the electron within the molecule, as the electron or charge delocalization is considered to be a significant stabilizing factor. For example, tertiary carbonium ion is more stable than that of primary and secondary. For the same reason allyl and

benzyl carbonium ion, carbanion ions, and radicals demonstrate great stability. Recently, the ultraviolet absorption spectrum of cyanine dyes was explained, following the current example of a particle in a box. Figure 4-3 displays the energy of the lowest five levels of the particle, according to Eq. (4-10).

In case of a particle moving in three-dimensional orientation, the energy model will be as follows:

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \quad (4-11)$$

where a , b , and c are the lengths of the three-dimensional box. However for the cubic box, the energy model will be represented by the following equation:

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2] \quad (4-12)$$

4.2.1. Example

Calculate the energy difference between the lowest two energy levels for an electron ($m=9.1 \times 10^{-31}$ kg), confined to one- dimensional box, having a length of 4.0×10^{-10} m. What is the wavelength corresponding to spectral transitions between these levels?

According to Eq. (4-10),

$$E_1 = \frac{(6.626 \times 10^{-34})^2}{8(9.1 \times 10^{-31})(4.0 \times 10^{-10})^2} = 3.77 \times 10^{-19} \text{ J (Hint: } J = \frac{\text{kg m}^2}{\text{s}^2})$$

The energy of $n=2$ is just four times $n=1$, and the energy difference, therefore, three times this value.

$$\Delta E = E_2 - E_1 = 3 \times 3.77 \times 10^{-19} = 1.33 \times 10^{-18} \text{ J}$$

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34})(2.998 \times 10^8)}{1.33 \times 10^{-18}} = 1.76 \times 10^{-7} m$$

$$= 176 \text{ nm}$$

λ is the wavelength in the ultraviolet region.

4.3. TWO-PARTICLE RIGID-ROTOR

The main purpose of taking this problem is for solving and understanding the molecular rotation or microwave spectroscopy. The two-particle rigid-rotor with masses m_1 and m_2 , separated by a distance r , could represent the fixed distance between two nuclei, as elucidated in Figure 4-4. In other words, the real bond length is not fixed, which extends throughout the rotation process. The translation movement of the presented system could be treated as a whole, using the total mass of the two atoms. Whereas, the rotational motion of the particles could be achieved in terms of reduced mass (μ). The expression of μ can be derived as below:

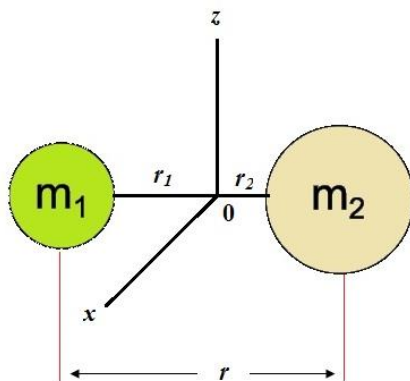


Figure 4-4. Two-particle rigid-rotor.

As the center of mass is located at the origin of the coordinate system (Figure 4-4), therefore:

$$m_1 r_1 = m_2 r_2 \quad (4-13)$$

$$r = r_1 + r_2 \quad (4-14)$$

Substituting r_2 of Eq. (4-14) into Eq. (4-13), one could get:

$$\begin{aligned} r_2 &= r - r_1 \\ m_1 r_1 &= m_2 (r - r_1) \\ m_1 r_1 &= m_2 r - m_2 r_1 \\ m_1 r_1 + m_2 r_1 &= m_2 r \\ r_1 (m_1 + m_2) &= m_2 r \end{aligned}$$

$$\text{So, } r_1 = \frac{m_2}{m_1 + m_2} r \quad (4-15)$$

Similarly, one could evaluate r_2 , as represented by the following formula:

$$r_2 = \frac{m_1}{m_1 + m_2} r \quad (4-16)$$

The moment of inertia I , concerning the line that passes through the center of mass of the presented system, can be represented as follows:

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (4-17)$$

substituting both r_1 and r_2 from Eqs. (4-15) and (4-16) into Eq. (4-17) gives:

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 \quad (4-18)$$

The expression between the brackets of Eq. (4-18) is equal to reduced mass (μ). Therefore,

$$I = \mu r^2 \quad (4-19)$$

As we mentioned at the beginning of this chapter, the solution of systems, using quantum mechanics started with the evaluation of the Hamiltonian function, thus,

$$H = T + U$$

For this system, the potential energy is equal to zero ($U=0$), due to the continual motion,

$$T = \frac{L^2}{2I} = \frac{L^2}{2\mu r^2} \quad (4-20)$$

where L is the angular momentum vector ($L = pr$); therefore, the Hamiltonian function for two-particle rigid-rotor can be written as:

$$H = \frac{p^2 r^2}{2\mu r^2} = \frac{p^2}{2\mu} = \frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) \quad (4-21)$$

The last three-dimensional equation is because the rotation process can be occurred in the three-axis, as described in Figure 4-5. Converting the achieved Hamiltonian function to the related Hamiltonian operator, using postulate II can be carried out as follows:

$$\hat{H} = \frac{-\hbar^2}{2\mu} \nabla^2 \quad (4-22)$$

The next step is to substitute the obtained Hamiltonian operator (Eq. (4-22)) in the Schrödinger equation (Eq. (3-20)), like the following:

$$\left(\frac{-\hbar^2}{2\mu}\nabla^2\right)\Psi = E\Psi \quad (4-23)$$

This differential equation must be solved mathematically for obtaining the wave function and the corresponding energy. For this example, the evaluation of the wave function is not that necessary, because the purpose of this function is to give an idea about the position, but we have already assumed the bond length from the center of the mass. However, Eq. (4-23) cannot be solved in the presented form and must be converted from the Cartesian coordinate to spherical polar coordinate, using the equations of chapter one (1-1, 1-2, and 1-3). The complete mathematical solution is quite long and is not sufficient to be discussed here. Furthermore, as in the above example of a particle in the box, the quantum number was formed for equation satisfaction purposes. Thus, the derived energy model of the two-particle rigid-rotor is represented by the following equation:

$$E_J = \frac{J(J+1)\hbar^2}{2\mu r^2} = \frac{J(J+1)\hbar^2}{2I} \quad J = 0, 1, 2, 3, \dots \quad (4-24)$$

where E_J is the rotational energy and J is the rotational quantum number. Eq. (4-24) can be rewritten in the following form, as the terms $\hbar^2$ and I can be represented by B constant.

$$E_J = BJ(J + 1) \quad J = 0, 1, 2, 3, \dots \quad (4-25)$$

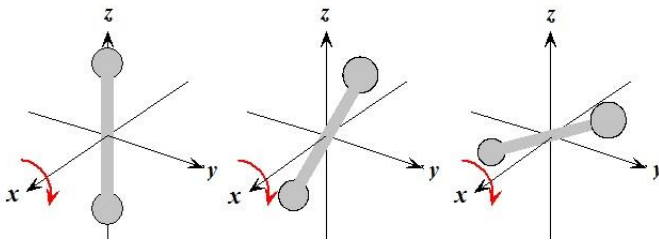


Figure 4-5. Rotation of the two-particle rigid-rotor around the x-axis.

The energy levels for the lowest five rotational energies are illustrated in Figure 4-6. It should be noted that not all molecules could be excited rotationally by microwave rays, only those having permanent electric dipole moments of polar molecules, can couple to the electric field of electromagnetic radiation.

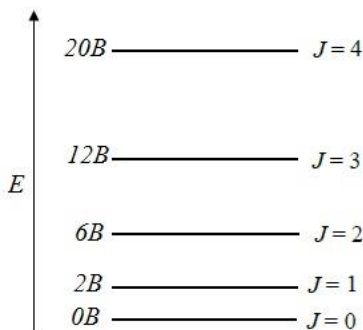


Figure 4-6. Rotational energy levels of two-particle rigid-rotor.

4.4. SIMPLE HARMONIC OSCILLATOR

The quantum mechanical treatment of the simple harmonic oscillator is quite necessary for understanding and modeling the molecular and crystal vibrations or infrared (*IR*) spectroscopy. In contrast to the previous example, the harmonic oscillator has potential energy, as the kinetic energy changes to potential throughout the vibration motion. However, the presented example was already shown in chapter one section 1.5.2.1, as the potential and kinetic energies were given by Eqs. (1-21) and (1-22), respectively. Therefore, the Hamiltonian function of the simple harmonic oscillator can be represented by the following equation:

$$H = \frac{p_x^2}{2m} + \frac{1}{2}kx^2 \quad (4-26)$$

Converting H function to its corresponding operator, using postulate II gives:

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad (4-27)$$

substituting this Hamiltonian operator into the Schrödinger equation (Eq. (3-20)) gives the following:

$$\left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right) \Psi = E\Psi \quad (4-28)$$

The solution of this differential equation gives the following eigenfunctions and eigenvalues for the lowest three levels:

$$\begin{aligned} \psi_0 &= \left(\frac{2a}{\pi} \right)^{1/2} e^{-ax^2} & E_0 &= \frac{1}{2} \hbar\omega \\ \psi_1 &= \left(\frac{2a}{\pi} \right)^{1/2} 2ax e^{-ax^2} & E_1 &= \frac{3}{2} \hbar\omega \\ \psi_2 &= \left(\frac{2a}{\pi} \right)^{1/2} (4a^2 x^2 - 1) e^{-ax^2} & E_2 &= \frac{5}{2} \hbar\omega \end{aligned}$$

The vibrational energy of the simple harmonic oscillator can be represented by the following general equation:

$$E_V = \left(V + \frac{1}{2} \right) \hbar\omega \quad V = 0, 1, 2, \dots \quad (4-29)$$

where V is the vibrational quantum number, ω is vibration frequency ($\omega = \sqrt{k/m}$), and $a = \pi/h\sqrt{km}$. The energy levels for the lowest eight rotational energies, according to Eq. (4-29) are demonstrated in Figure 4-7.

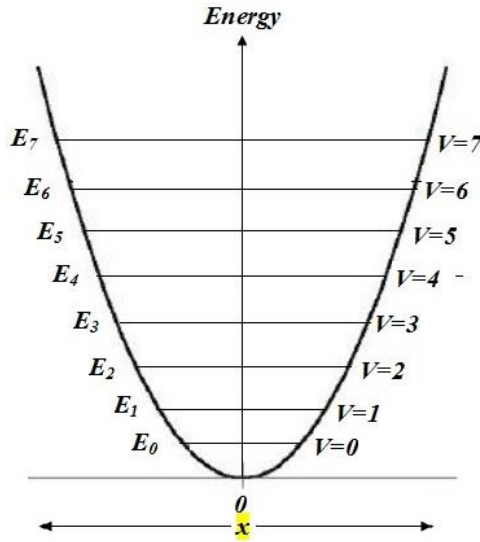


Figure 4-7. Vibrational energy levels of the simple harmonic oscillator.

It should be noted that the solution of this example by quantum theory (Eq. (2-19)) gives parallel vibrational energy, in contrast to that of quantum mechanics. However, the model of Sommerfeld quantization as could be presented by Eq. (4-30), is not acceptable in terms of the uncertainty principle. This is because at $x=0$, the energy is also equal to zero, and then one could determine precisely the position and the associated energy simultaneously.

$$E_V = V\hbar\omega \quad V = 0, 1, 2, \dots \quad (4-30)$$

4.5. THE HYDROGEN ATOM

The treatment of atoms by quantum mechanics is considered an essential task for solving the problems of both chemists and physicists. 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 atom was already evaluated in chapter one Eq. (1-41), which can be represented as follows (supposedly, the nucleus is fixed):

$$H = \frac{1}{2m_e} (p_x^2 + p_y^2 + p_z^2) + \frac{-Ze^2}{4\pi\epsilon_0 r} \quad (4-31)$$

where Z is the atomic number, which is equal to unity for the H atom. Converting the Hamiltonian function to its corresponding operator, using postulate II gives:

$$\hat{H} = \frac{-\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (4-32)$$

substituting this Hamiltonian operator into the Schrödinger equation (Eq. (3-20)), one can get:

$$\left(\frac{-\hbar^2}{2m_e} \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \right) \Psi = E\Psi \quad (4-33)$$

$$\begin{aligned} \frac{-\hbar^2}{2m_e} \left[\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right] - \frac{Ze^2 \Psi}{4\pi\epsilon_0 r} &= E\Psi \quad (4-34) \times -\frac{2m_e}{\hbar^2} \\ \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{Ze^2 \Psi}{4\pi\epsilon_0 r} \frac{2m_e}{\hbar^2} + \frac{2m_e}{\hbar^2} E\Psi &= 0 \end{aligned} \quad (4-35)$$

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

Again, similar to Eq. (4-23) for rigid-rotor, Eq. (4-36) cannot be solved, as the Cartesian coordinate is unable to describe such a two-particle system. The transformation of the last equation to spherical coordinates as presented in Figure 4-8, using Eqs. (1-1), (1-2) and (1-3), yields:

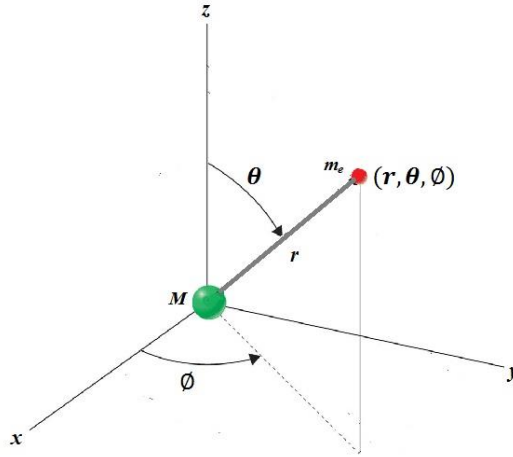


Figure 4-8. Spherical coordinates for describing the hydrogen atom.

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

It was found that the mathematical treatment of the last equation (4-37) also cannot give a solution. The reason for this phenomenon could be attributed to that the wave function (ψ) cannot cover all the positions of atom particles. In other words, the supposed spherical shape of an atom cannot be described by one position and depends on three parameters (r , θ , and ϕ). Therefore, in order to solve this problem, the ψ of Eq. (4-37) should be written as a product of three functions, one dependent on r , one dependent on θ and one dependent on ϕ , as presented by the following:

$$\psi(r, \theta, \phi) = R_{(r)} \Theta_{(\theta)} \Phi_{(\phi)} \quad (4-38)$$

Each of these three suggested wavefunctions (R , Θ , and Φ) needs the corresponding Hermitian operators to be substituted in Eq. (4-37). Thus, $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ can be considered the corresponding operators for the wavefunctions R , Θ , and Φ , respectively. Therefore, when these

wavefunctions and their related operators are substituted in Eq. (4-37), three ordinary differential relations emerge. Interestingly, each of these three equations can mathematically be solved with a quantum number for satisfying each of these relations. Hence, the atoms have three integer quantum numbers, in contrast to only one with other systems. In other words, equation of $\hat{H}$ and R gives the principal quantum number n ($n=1, 2, 3, \dots$), equation of $\hat{L}^2$ and Θ gives orbital quantum number l [$l=0, 1, 2, \dots, (n-1)$], and equation of $\hat{L}_z$ and Φ gives magnetic quantum number m_l ($m_l=0, \pm 1, \pm 2, \dots, \pm l$). Letter symbols are associated with orbital quantum number l , as follows:

$$l = 0 \ 1 \ 2 \ 3$$

Symbol $s \ p \ d \ f$

The energy (E) or the eigenvalue of the hydrogen atom was estimated from the first equation of $\hat{H}$ and R , which is parallel to that of Bohr atom (Eqs. (2-7) and (2-8)). In other words, quantum theory successfully derived the energy model for the hydrogen atom, as confirmed by quantum mechanics.

The total or real wavefunction (Eq. (4-38)) was estimated for the lowest three principal quantum numbers, as given in Table 4-1. The resulted wavefunction models may indicate 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. On the other hand, the plot of the radial wavefunctions versus inter-atomic distance (Figure 4-9 (a)), does not give a physical definition about the position of each orbital, as the function $R(r)$ cannot give an idea about the probability of finding the electron somewhere. Whereas, the plot of the probability density for finding the electrons ($r^2 R_{(r)}^2$) versus r , could give such valuable information about the atomic structure, as clearly shown in Figure 4-9 (b).

Table 4-1. The wavefunctions of the hydrogen atom for the lowest three principal quantum numbers^{*^}

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	$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} (6 - \sigma) e^{-\sigma/3} \cos \theta$
3	1	± 1	$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} (6 - \sigma) e^{-\sigma/3} \sin \theta \cos \phi$ $\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} (6 - \sigma) e^{-\sigma/3} \sin \theta \sin \phi$
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	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2 \theta \cos 2\phi$ $\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2 \theta \sin 2\phi$

^{*} $a_0 = \frac{h^2(4\pi\epsilon_0)}{m_e e^2}$ $\wedge \sigma = \frac{Z}{a_0} r$.

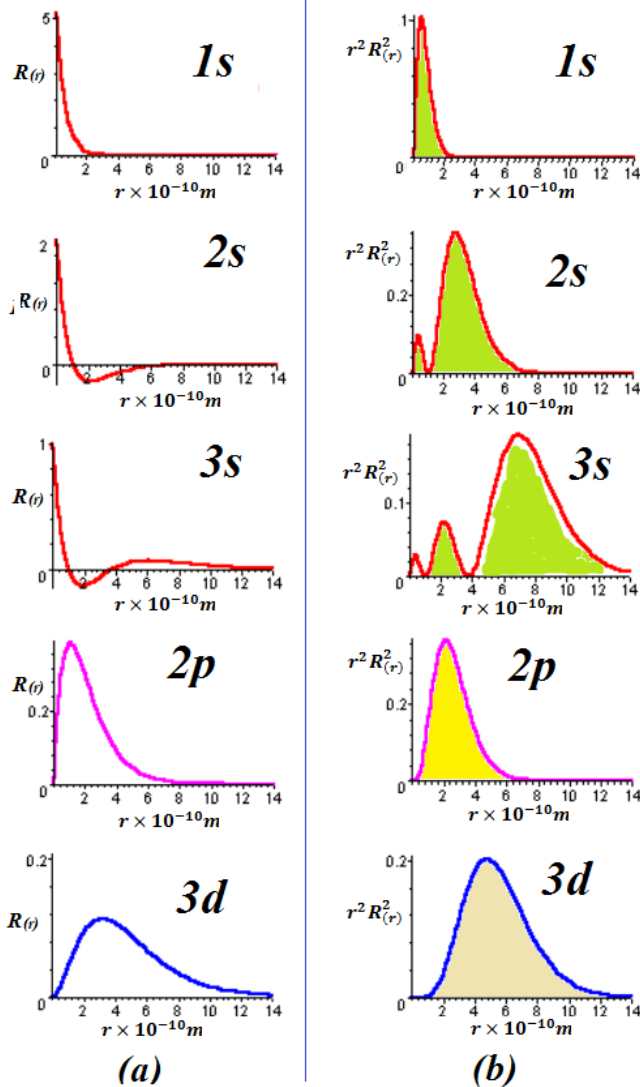


Figure 4-9. (a) The electronic radial wave function $R(r)$ for a hydrogen atom. (b) The probability density for finding the electrons $r^2 R^2(r)$ for a hydrogen atom (Adopted from ref. <http://staff.mbi-berlin.de/hertel/physik3/chapter8/8.3html/01.htm>).

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

$$W^2 = \theta^* \theta \Phi^* \Phi \quad (4-39)$$

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. The shapes of $1s$, $2p$, and $3d$ orbitals for a hydrogen atom evaluated from W^2 , are shown in Figure 4-10. It should be noted that θ and ϕ angles depend primarily on the values of orbital quantum number l . When l is equal to zero, one could notice that in s orbitals, the angular wave function is constant and independent of these angles. Thus, this function will provide a spherical shape of this orbital.

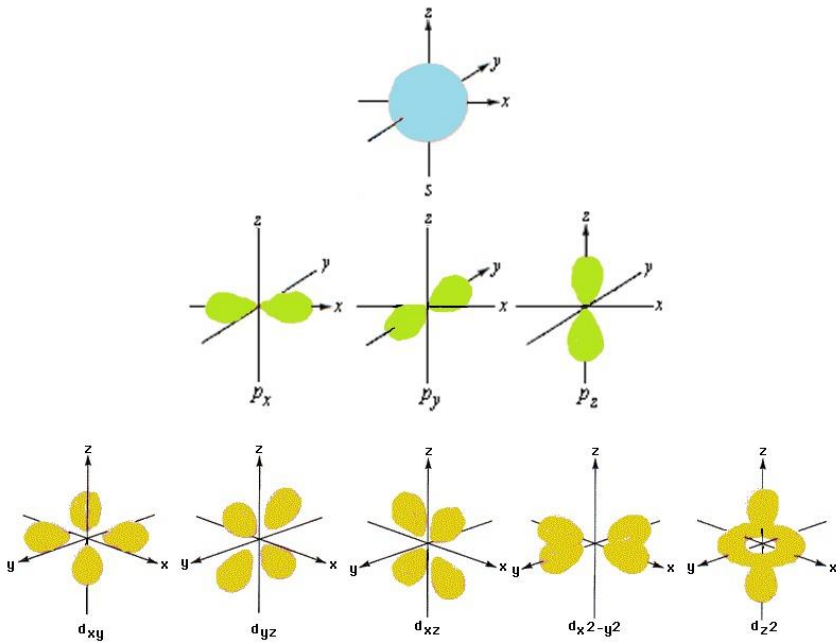


Figure 4-10. Shapes of $1s$, $2p$, and $3d$ orbitals for a hydrogen atom from an angular part of the wavefunction $W(\theta, \Phi)$.

Indeed, the shapes of orbitals (Figure 4-10) can be proved experimentally by nuclear magnetic resonance (NMR) measurements, throughout the shielding phenomenon. In other words, the shielding of

the nucleus decreases with increasing the p-character of surrounding electrons. For example, the shielding of nuclei takes the following sequence, $H^1 > C^{13} > N^{15} > F^{19}$.

4.6. THE PROBLEM OF THE SCHRÖDINGER EQUATION WITH NON-HYDROGENLIKE ATOMS

The above treatment of hydrogen atom is somewhat considered as an exact solution, which also can be used for hydrogenlike atoms, such as He^+ ion. Now, if we do not assume that the nucleus of the hydrogen atom is fixed as in a real state, then, the Hamiltonian operator of this atom can be written as follows:

$$\hat{H} = \frac{-\hbar^2}{2M} \nabla_n^2 - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \quad (4-40)$$

where ∇_n^2 and ∇_e^2 are the Laplacian operators for nucleus and electron, respectively. Following the above solution of the hydrogen atom, one could find that each Laplacian operator needs three dynamical operators ($\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$) with three differential equations. Therefore, six dynamical operators are needed in order to solve this problem. In this special case, there are three dynamical operators, representing the kinetic energies of the center of mass (nucleus), concerning the conservation of energy at three-axis ($\hat{Y}_x$, $\hat{Y}_y$, and $\hat{Y}_z$). Thus, one could have 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. However, for a system possessing three particles such as helium (He) atom, nine dynamical operators needed, as an essential mathematical requirement for solving this system. However, only six dynamical operators are available ($\hat{H}$, $\hat{L}^2$, $\hat{L}_z$, $\hat{Y}_x$, $\hat{Y}_y$, and $\hat{Y}_z$), which are not enough from a mathematical point of view. If one supposes that the nucleus is

fixed in order to neglect one of three Laplacian operators, then, only three dynamical operators will remain ($\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$), as those operators belonging to the kinetic energy of the center of mass ($\hat{Y}_x$, $\hat{Y}_y$, and $\hat{Y}_z$) will be eliminated. This is due to that the operators $\hat{Y}_x$, $\hat{Y}_y$, and $\hat{Y}_z$ must be equal to zero, as they only depend on the kinetic energy of the nucleus, which considered as the slowest particle and then can be accepted as fixed.

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

4.7. EXERCISES

1. Calculate the energy difference between $n=1$ and $n=2$ levels for marble of mass 1 g , confined in a one-dimensional box with a length of 0.1 m . What is the wavelength corresponding to a spectral transition between these levels?
2. Why microwave oven heats water, but not air?
3. Why the Schrödinger equation cannot exactly solve the systems that have more than two particles?
4. Is there any potential energy in the simple harmonic oscillator?
5. Why the solution of hydrogen atom using quantum mechanics is giving three separated quantum numbers, in contrast to other problems that they have given only one quantum number?
6. How one could prove practically the correctness of three-dimensional shapes of $1s$, $2p$, and $3d$ orbitals?
7. Is the position of the particle in a box depending on the energy level?

Chapter 5

APPROXIMATE METHODS FOR TREATING MULTI-ELECTRON ATOMS

5.1. INTRODUCTION

It is clearly stated at the end of the preceding chapter that the Schrödinger equation can only exactly solve systems with two particles, such as hydrogen like atoms. Therefore, approximate methods are necessary for solving atoms with more than two electrons. There are two methods for such purposes:

1. Variation theory
2. Perturbation theory

Noting that the second method, perturbation depends merely on the first method, which therefore the second method could be considered as the developed ones.

Two main problems will appear with many-electron atoms. These imply that under the uncertainty principle, the many electron-electron

repulsions and also the distinguishing between electrons must be avoided.

5.2. VARIATION THEORY

The variation principle can be defined simply as “the calculated energy of a system must always be higher or equal to its exact energy”. This can be applied, using postulate IV as presented by the following model:

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

where E is the calculated energy and E_o is the exact or real energy of the system. If one could imagine simply that the expression of the last equation is belonging to constant values rather than functions and operator, then one gets the minimum value of the energy throughout variation of the values of constants. This could give the reason for calling the variation word for this method, which is parallel to the minimization term, used by scientists.

However, such a job of variation principle is quite complex in quantum mechanics, which may be illustrated as the following. As a consequence of the variation principle is that if the trial Ψ depends on several arbitrary parameters, $\lambda_1, \lambda_2, \dots, \lambda_n$, therefore,

$$\Psi = \Psi(\mathbf{r}; \lambda_1, \lambda_2, \dots, \lambda_n) \quad (5-2)$$

where $\mathbf{r}$ represents the dependence of the wavefunction Ψ on the coordinates of electrons. The values of these arbitrary parameters can be chosen in order to obtain the lowest possible (the most accurate) value of the energy. Moreover, the energy is a function of these parameters, and

the values that give the minimized value of energy can be obtained throughout solving the following equation:

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

On the other hand, the common type approximate wave function Ψ , for a system of n electrons can be expressed in term of the linear combination of atomic orbitals:

$$\Psi = C_1\phi_1 + C_2\phi_2 + \dots + C_n\phi_n = \sum_{j=1}^n C_j\phi_j \quad (5-4)$$

where the coefficients C_j are parameters and ϕ_j are N -electron functions, which can be considered as Ψ of each electron. According to postulate IV, the corresponding energy of this Ψ is:

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

where $H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau$ (5-6), and

$$S_{ij} = \int \phi_i^* \phi_j d\tau \quad (5-7)$$

The minimization of the last energy, concerning the corresponding n coefficients, can give a set of n (secular) equations, as represented by the following:

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

The optimum solution of the last equation is building up a secular determinant of the following format:

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

The solution of this polynomial determinant of degree and roots of n , gives the n -electron energy levels with values that are not necessarily all different, due to the presence of degeneracy,

$$E_1 \leq E_2 \leq E_3 \leq \dots \leq E_n$$

There is a corresponding wavefunction for each of these energies (E_i),

$$\Psi_i = \sum_{j=1}^n \phi_j C_{ji} \quad (5-10)$$

By applying the conditions of the normalization and orthogonality for the resulted wavefunctions, one could evaluate the values of E_i . The lowest root E_1 is considered as approximate ground-state energy with corresponding approximate wavefunction Ψ_1 . If E_i^0 is the exact or real energy of the i th state, then $E_i \geq E_i^0$, but $E_i = E_i^0$ if Ψ_i is the exact wavefunction for the i th state. It should be noted that the increase in the number of arbitrary variational parameters in a wavefunction, increases the accuracy of the corresponding energy.

5.3. TREATMENT OF HELIUM ATOM USING THE VARIATION THEORY

In general and in order to solve problems, using the variation theory, one has to choose trial variational wave function, $\Psi(\omega)$, and trial variational energy, $E(\omega)$, which can be estimated according to Eq. (5-1).

This is in addition to one or more variational variables or parameters (ω), as mentioned previously (Eq. (5-2)), and then using the following equation for minimization task.

$$\frac{dE(\omega)}{d\omega} = 0 \quad (5-11)$$

Hence, the model of variation theory of Eq. (5-1) can be rewritten in this format:

$$E(\omega) = \frac{\int \psi^*(\omega) \hat{H} \psi(\omega) d\tau}{\int \psi^*(\omega) \psi(\omega) d\tau} \geq E_0 \quad (5-12)$$

The minimization process of trial variational energy ($E(\omega)$) will be carried out, using Eq. (5-11), and the smallest value will be corresponding to the energy of the system, according to the variation principle.

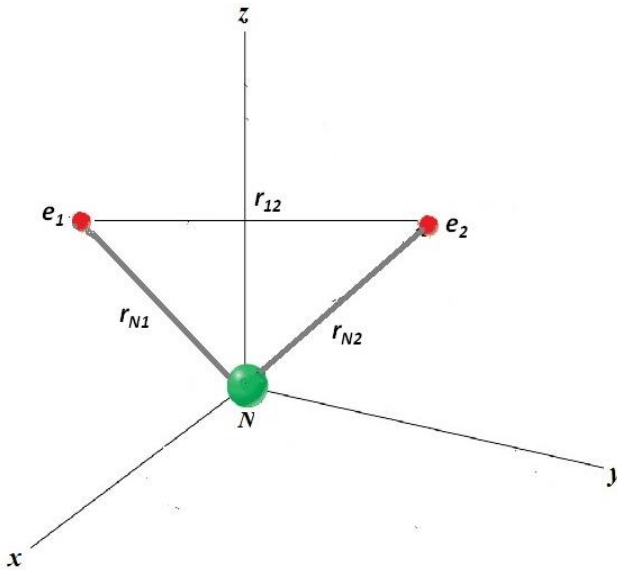


Figure 5-1. Spherical coordinates for describing the helium atom.

The helium atom is the next simplest system of the atom after the treatment of hydrogenlike atoms. Figure 5-1 demonstrates this atom, where e_1 and e_2 are the two electrons, N is the nucleus, r_{N1} and r_{N2} are the distances between each of e_1 and e_2 with N , respectively, and r_{12} is the distance between electrons. If one supposes that the nucleus is fixed, the Hamiltonian operator can be represented by Eq. (5-13).

$$\hat{H} = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_{N1}} - \frac{2e^2}{4\pi\epsilon_0 r_{N2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (5-13)$$

where ∇_1^2 and ∇_2^2 are the Laplacian operators for e_1 and e_2 , respectively. Eq. (5-13) can be rewritten in this format:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_{N1}} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_{N2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (5-14)$$

The Hamiltonian operator of this equation is the sum of two hydrogen like atoms, in addition to the electron-electron repulsion term, e^2/r_{12} . At the same time, both electrons of a helium atom in the ground state exist in Ψ_{1s} orbital. The equation of Ψ_{1s} for the hydrogen atom is already evaluated in the previous chapter (Table 4-1), which can be rewritten as the following:

$$\Psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Z}{a_0} r} \quad (5-15)$$

However, the effective charge of the hydrogen nucleus certainly differs from that of the helium atom. Therefore, one could consider the effective charge is a good variable for variation method, as the variational wavefunction for one electron could be presented in this format:

$$\Psi_{1s}(\omega) = \left(\frac{\omega^3}{\pi a_0^3} \right)^{1/2} e^{-\omega r/a_0} \quad (5-16)$$

As Φ is the trial wavefunction for 1s orbital of a helium atom, the product of the two electrons 1 and 2, is as follows:

$$\Phi = \Psi_{1s}(\omega)(1) \cdot \Psi_{1s}(\omega)(2) \quad (5-17)$$

substituting Eq. (5-16) by both electron in that of Eq. (5-17) yields:

$$\Phi = \left(\left(\frac{\omega^3}{\pi a_0^3} \right)^{1/2} e^{-\omega r_{N1}/a_0} \right) \left(\left(\frac{\omega^3}{\pi a_0^3} \right)^{1/2} e^{-\omega r_{N2}/a_0} \right) \quad (5-18)$$

On the other side, the variational variable (ω) should also be added to the Hamiltonian operator of Eq. (5-14), in order to make it more suitable for helium atom, as there is a difference in the charge of the nucleus in addition to two electrons, like the following:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\omega e^2}{4\pi\epsilon_0 r_{N1}} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\omega e^2}{4\pi\epsilon_0 r_{N2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{(2-\omega)e^2}{4\pi\epsilon_0 r_{N1}} - \frac{(2-\omega)e^2}{4\pi\epsilon_0 r_{N2}} \quad (5-19)$$

The last two additional terms (sixth and seventh) were added because the variational variable (ω) in second and third terms is not necessarily equal to the atomic number 2. So, there is an extra charge, which was initially 2 that has been added as two additional terms for correction purposes. The first two terms of Eq. (5-19) can be considered as an effective Hamiltonian operator for electron 1, and similarly, the third and fourth terms for electron 2 are as follows:

$$\hat{H}_1^{eff} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\omega e^2}{4\pi\epsilon_0 r_{N1}} \quad (5-20)$$

$$\hat{H}_2^{eff} = -\frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\omega e^2}{4\pi\epsilon_0 r_{N2}} \quad (5-21)$$

Thus, the Hamiltonian operator of Eq. (5-19) can be represented in five terms as:

$$\hat{H} = \hat{H}_1^{eff} + \hat{H}_1^{eff} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{\omega e^2}{4\pi\epsilon_0 r_{N2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{(2-\omega)e^2}{4\pi\epsilon_0 r_{N1}} - \frac{(2-\omega)e^2}{4\pi\epsilon_0 r_{N2}} \quad (5-22)$$

Now replacing Eqs. (5-18) and (5-22) in Eq. (5-12), one could get:

$$E(\omega) = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau} \quad (5-23)$$

This followed by some complex mathematical treatment, using some partitions of this equation, including the normalization of wavefunctions and takes the minimum value of trial energy, according to the following equation:

$$\frac{d\left(\frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}\right)}{d\omega} = 0 \quad (5-24)$$

The minimum trial variational energy is corresponding to the energy of the helium atom. The results show that the optimum value of a variational variable (ω) is equal to 27/16, and the trial variational energy of helium atom is equal to -1.241×10^{-17} J, in contrast to the exact energy, which is equal to -1.266×10^{-17} J.

5.4. PERTURBATION THEORY

The main principle of this theory is the comparison between an unknown system with that of a related known one. It can be defined as “it is often the case that $\hat{H}$ for the system of interest differs only slightly from $\hat{H}$ of the related system”. For example, imagine there is a molecule

in a weak electric field for which the Hamiltonian operator ($\hat{H}$) can be represented as:

$$\hat{H} = \hat{H}_0 + \lambda V \quad (5-25)$$

where $\hat{H}_0$ is the Hamiltonian operator of the known or unperturbed system for the molecule in the absence of the electric field, and λV is a small perturbation term, which expresses the interaction between the molecule with the electric field, whereas λ is the perturbation parameter, which is considered as a measure of the strength of the perturbation such as the strength of the electric field. Thus, the principle of perturbation theory can be explained in terms of the unknown system, which may be considered as the known system in the pretreated state. It should be noted that the previous variation method is an essential part of perturbation theory, which the later can be relatively considered as the advanced method.

However, the Schrödinger equation of the known system (unperturbed) that eigenvalue and eigenfunction of $\hat{H}_0$ are known, is represented by Eq. (5-26).

$$\hat{H}_0 \psi_n^0 = E_n^0 \psi_n^0 \quad (5-26)$$

Whereas, the Schrödinger equation of the unknown system (perturbed), where eigenvalue and eigenfunction of $\hat{H}$ are unknown, can be represented as follows:

$$\hat{H} \psi_n = E_n \psi_n \quad (5-27)$$

The expressions of the last equation will follow the limit of the above perturbation parameter $\lambda \rightarrow 0$, $\hat{H} \rightarrow \hat{H}_0$, $E_n \rightarrow E_n^0$, and $\psi_n \rightarrow \psi_n^0$. The basic proposition of perturbation theory is that the eigenvalue and eigenfunction of the unknown or perturbed state can be extended as

power series in λ , in relation to corresponding energy and wavefunction of the unperturbed or known state (Eqs. (5-28) and (5-29)).

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots \quad (5-28)$$

$$\Psi_n = \Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots \quad (5-29)$$

Noting that these models are valid for the whole range of values of λ between zero and the value of interest, the quantity E_n^i is called the i th-order energy, and Ψ_n^i is the i th-order wavefunction. By substituting the expressions of Eqs. (5-25), (5-28) and (5-29) into the Schrödinger equation of the perturbed system (Eq. (5-27)), one could get:

$$(\hat{H}_0 + \lambda V)(\Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)(\Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots) \quad (5-30)$$

When $\lambda=0$, this equation will reduce to unperturbed values as Eq. (5-26), which called the zeroth-order equation, and can be represented as follows:

$$(\hat{H}_0 - E_n^0)\Psi_n^0 = 0 \quad (5-31)$$

Eq. (5-30) can be expanded, and comparing the coefficients of each power of λ could give an infinite series of simultaneous equations. The first- and second-order equations are:

$$(\hat{H}_0 - E_n^0)\Psi_n^1 + (V - E_n^1)\Psi_n^0 = 0 \quad (5-32)$$

$$(\hat{H}_0 - E_n^0)\Psi_n^2 + (V - E_n^1)\Psi_n^1 - E_n^2\Psi_n^0 = 0 \quad (5-33)$$

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

$$E_n^1 = \int \Psi_n^{0*} V \Psi_n^0 d\tau \quad (5-34)$$

$$E_n^2 = \int \Psi_n^{0*} V \Psi_n^1 d\tau \quad (5-35)$$

and, in general

$$E_n^i = \int \Psi_n^{0*} V \Psi_n^{i-1} d\tau \quad (5-36)$$

The energy of first-order can be expressed by the following combination of Eq. (5-28) and (5-34):

$$E_n^0 + \lambda E_n^1 = \int \Psi_n^{0*} (\hat{H}_0 + \lambda V) \Psi_n^0 d\tau = \int \Psi_n^{0*} \hat{H} \Psi_n^0 d\tau \quad (5-37)$$

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

$$E_n^2 = \int \Psi_n^{0*} (\hat{H}_0 - E_n^0) \Psi_n^1 d\tau + 2 \int \Psi_n^{0*} V \Psi_n^1 d\tau \quad (5-38)$$

$$E_n^3 = \int \Psi_n^{1*} (V - E_n^1) \Psi_n^1 d\tau \quad (5-39)$$

The first-order wavefunction can be calculated, using the variation principle along with the second-order energy Eq. (5-38), through replacing Ψ_n^1 by an approximate function Φ , like the following:

$$E_n^2 \leq W = \int \Phi^* (\hat{H}_0 - E_n^0) \Phi d\tau + 2 \int \Psi_n^{0*} V \Phi d\tau \quad (5-40)$$

Thus, the approximate second-order energy can be minimized concerning the variation of Φ , and the calculated approximate first-order wavefunction could then be used for estimating the approximate value of the third-order energy (Eq. (5-39)).

5.5. Electron Spin

The line spectra of atoms exhibit a fine structure, which is not clear from a theoretical point of view. For instance, the sodium D-lines of two closely spaced identical lines, indicate the duplication of the number of states that are available for the valence electron. Such a phenomenon does not exist in the line spectrum of hydrogen, helium, and neon, but also found in several metals, such as mercury. Therefore, the spin eigenfunction was not involved throughout the solution of the hydrogen atom, using the Schrödinger equation.

On the other hand, in 1922 Stern and Gerlach showed throughout their experiment that silver atoms deflected up or down, depending on their spin when traveling through an inhomogeneous magnetic field. Stern–Gerlach experiment also demonstrated the quantization of angular momentum. In 1925, Uhlenbeck and Goudsmit suggested the existence of an additional new intrinsic property of particles, which behaves similar to angular momentum. Later on, this new property was named spin by Pauli. Uhlenbeck and Goudsmit proposed that the spin of the particle behaves like angular momentum, possessing an associated magnetic moment.

In general, the two possible spin eigenfunctions for an electron can be represented by α and β , under the following equations:

$$\hat{S}_z \alpha = \frac{1}{2} \hbar \alpha \quad (5-41)$$

$$\hat{S}_z \beta = -\frac{1}{2} \hbar \beta \quad (5-42)$$

where $\hat{S}_z$ is the spin angular momentum operator in the z-direction, α and β are the spin eigenfunctions with spin up and down, respectively; $1/2$ and $-1/2$ are the electron spin, which constituted of upward and downward directions, respectively.

Thus, the total wavefunction for the electron (Ψ) can be expressed in this format:

$$\Psi = \Psi_i \sigma \quad (5-43)$$

where Ψ_i is the space or spatial function, and σ is the spin function.

5.6. PAULI EXCLUSION PRINCIPLE

The distinguishing issue that forbidden by the uncertainty principle plays an important role when one deals with a system of interacting identical particles. Such a system is found when determining the wavefunction for many-electron atoms, as the electrons are considered as typical example of identical particles.

Let take the ground state of helium atom as the simplest example for many-electron atoms. In this system, the electrons 1 and 2 are both in $1s$ orbital with different spin functions. According to Eq. (6-18), the wave function of this atom as the multiplication of spatial functions by spin functions gives:

$$\Psi = 1s(1)1s(2)\alpha(1)\beta(2) \quad (5-44)$$

Indeed, Eq. (5-44) is not satisfactory, which contradicts the uncertainty principle, as the last equation implies that electrons 1 and 2 can be distinguished from each other concerning their spins. In other words, Eq. (5-44) indicates the upward and downward directions of the spin for electron 1 and electron 2, respectively, as clear distinguishing between those identical molecules. Thus, there is another probability, which also is not acceptable by the Heisenberg principle (uncertainty principle) as follows:

$$\Psi' = 1s(2)1s(1)\alpha(2)\beta(1) \quad (5-45)$$

Eqs. (5-44) and (5-45) look like an interchange is made between electrons 1 and 2. However, in order to avoid the distinguishing phenomenon, addition or subtraction of Eqs. (5-44) and (5-45) must be made as to the following:

$$\Psi_1 = \frac{1}{\sqrt{2}} [1s(1)1s(2)\alpha(1)\beta(2) + 1s(2)1s(1)\alpha(2)\beta(1)] \quad (5-46)$$

$$\Psi_2 = \frac{1}{\sqrt{2}} [1s(1)1s(2)\alpha(1)\beta(2) - 1s(2)1s(1)\alpha(2)\beta(1)] \quad (5-47)$$

where $1/\sqrt{2}$ is the normalization constant that is required for normalization. Ψ_1 is called symmetric because the exchange of electrons 1 and 2 does not change the value of the function. Whereas, Ψ_2 is appointed anti-symmetric as the exchange of electrons 1 and 2 does change the value of the function. In other words, the magnitude of subtraction of Eq. (5-45) from Eq. (5-44) does not equal to that of Eq. (5-44) from (5-45), as shown:

$$\begin{aligned} & [1s(1)1s(2)\alpha(1)\beta(2) - 1s(2)1s(1)\alpha(2)\beta(1)] = \\ & -[1s(2)1s(1)\alpha(2)\beta(1) - 1s(1)1s(2)\alpha(1)\beta(2)] \end{aligned} \quad (5-48)$$

Although, both wavefunctions of symmetric and anti-symmetric are correct, concerning the uncertainty principle, the helium atom in its ground state just has one correct wavefunction. In 1925, Pauli experimentally shows that only the anti-symmetric wavefunction (Eq. (5-47)) correctly describes the helium atom. At the same time, the symmetric wavefunction is not correct and must be excluded. Therefore, this achievement is referred to as the exclusion principle, or the Pauli principle, which can be defined as “no two electrons in an atom or molecules can be in the same state or configuration simultaneously”. This

important principle can simply be proved by that if the two electrons of helium atom have the same spin function, therefore the wavefunction will be equal to zero (Eq. (5-47)), as there is no atom.

The above treatment of helium atom will be quite complex for other many-electron atoms, as the probability of avoiding the distinguishability increases. For example, the treatment of lithium and boron atoms gives 6 and 24 equations, respectively. This problem was mathematically solved by Slater throughout his determinant, which will be given later. In 1929, Slater solved this problem by developing a mathematical method for constructing the anti-symmetric wavefunction, using determinants.

It should be noted that the Pauli exclusion principle is quite useful in chemistry as one could say that there are no two electrons in an atom that have the same quantum numbers n , l , m_l and m_s (m_s is the spin quantum number or electron spin of the values $1/2$ and $-1/2$).

Not all particles are satisfying with anti-symmetric wavefunction. Particles with half-integer spin ($1/2$, $3/2$, $5/2$, ...), all require anti-symmetric wavefunctions, which are referred to as “fermions”. Whereas, particles with integer spin (0 , 1 , 2 , ...) all require symmetric wavefunctions, which are referred to as “bosons”. Fermions are considered as the fundamental particles of matter, whereas, bosons are considered as the force carriers. Furthermore, fermions are satisfied with a kind of statistics called “Fermi-Dirac statistics”; on the other hand, bosons follow different statistics law, called “Bose-Einstein statistics”.

5.6.1. The First Excited State of the 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. In this example, the treatment of each of the spatial and spin wavefunctions will be separated, and then added to each other by the multiplication process. In order to avoid the

distinguishability for the two electrons in spatial part, the same treatment as above for helium atom in its ground state will give the following:

$$\frac{1}{\sqrt{2}} [1s(1)2s(2) + 1s(2)2s(1)] \quad (5-49)$$

$$\frac{1}{\sqrt{2}} [1s(1)2s(2) - 1s(2)2s(1)] \quad (5-50)$$

Noting that there is no concern about the exclusion principle at this stage because the above wavefunctions are considered not complete, as needed to be combined with spin functions. On the other side, as the two electrons are in different orbitals, it is possible to have the same spin direction or opposite, according to the following four possible spin functions.

$$\alpha(1)\alpha(2) \quad (5-51)$$

$$\beta(1)\beta(2) \quad (5-52)$$

$$\alpha(1)\beta(2) \quad (5-53)$$

$$\alpha(2)\beta(1) \quad (5-54)$$

There is no problem with those Eqs. (5-51) and (5-52) from a distinguishability point of view, in contrast to those of Eqs. (5-53) and (5-54). Therefore, similar to the spatial part, the distinguishability of the last two equations can be treated for achieving the following two wavefunctions.

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (5-55)$$

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (5-56)$$

Each of the four Eqs. (5-51), (5-52), (5-55), and (5-56) are correct from the uncertainty principle point of view, which will be used to multiply each of the two spatial functions (Eqs. (5-49) and (5-50)). Thus, eight wavefunctions should be obtained, but only the anti-symmetric will be taken, according to the exclusion principle. The results show that there are four neglected symmetrical wavefunctions with four acceptable anti-symmetric wavefunctions, representing the first excited state of helium atom as the following:

$$\Psi_1 = \frac{1}{2}[1s(1)2s(2) + 1s(2)2s(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (5-57)$$

$$\Psi_2 = \frac{1}{2}[1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (5-58)$$

$$\Psi_3 = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)]\alpha(1)\alpha(2) \quad (5-59)$$

$$\Psi_4 = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 1s(2)2s(1)]\beta(1)\beta(2) \quad (5-60)$$

The spatial part of Ψ_1 is symmetric, but the whole function is anti-symmetric due to the negative sign of the spin part, which is not symmetric. In contrast, the spatial part of Ψ_2 , Ψ_3 , and Ψ_4 are all anti-symmetric, but their spin parts are symmetric, which also makes the wavefunctions anti-symmetric. Thus, one (singlet) wavefunction (Ψ_1) of symmetric spatial part and three (triplet) wavefunctions (Ψ_2 , Ψ_3 , and Ψ_4) of anti-symmetric spatial parts are found. These indicate that the energy level of the singlet state is differing (higher) from the energy level of the wavefunctions of the triplet state, as they degenerate.

When the helium atom is at its ground state, the two electrons of $1s$ are paired and the resultant electron spin is zero. However, at first excited state when one electron is in the $2s$ orbital, the electrons may be paired (anti-parallel), and as they are in the singlet state, represented by Ψ_1 wavefunction, or if unpaired (parallel), they are in the triplet state,

represented by Ψ_2 , Ψ_3 , and Ψ_4 wavefunctions. However, in the presence of a magnetic field, no split can be detected in the singlet energy level, but the triplet energy level is split into three distinguished levels. This phenomenon is due to that the three wavefunctions (Ψ_2 , Ψ_3 , and Ψ_4) of triplets have the spins in the z-direction of 0, +1, and -1, respectively, as having different interacting modes with the external magnetic field.

5.7. SLATER DETERMINANT

In 1929, Slater solved the complex problem of the exclusion principle for many-electron atoms by developing a mathematical method for constructing the anti-symmetric wavefunction, using determinants. For example, the anti-symmetric wavefunction of the helium atom at its ground state can be represented by the following model:

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \quad (5-61)$$

The results of this model are similar to that of Eq. (5-47), representing the anti-symmetric wavefunction of this atom. In general, the Slater determinant introduces the elements of the same spin-orbital in a given column, while the elements of the same electron are in the given row. The wavefunction of the N-electron system can be represented by the Slater determinant in the following general format:

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \phi_3(x_1) & \cdots & \cdots & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \phi_3(x_2) & \cdots & \cdots & \phi_N(x_2) \\ \phi_1(x_3) & \phi_2(x_3) & \phi_3(x_3) & \cdots & \cdots & \phi_N(x_3) \\ \vdots & \vdots & \vdots & & & \vdots \\ \vdots & \vdots & \vdots & & & \vdots \\ \phi_1(x_N) & \phi_2(x_N) & \phi_3(x_N) & \cdots & \cdots & \phi_N(x_N) \end{vmatrix} \quad (5-62)$$

where $\phi_i(x_i)$ is the one-electron function, representing both the spatial ϕ_i and spin x_i parts. For lithium atom (N=3) for example, the Slater determinant can be represented in the following format:

$$\Psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \phi_3(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \phi_3(x_2) \\ \phi_1(x_3) & \phi_2(x_3) & \phi_3(x_3) \end{vmatrix} \quad (5-63)$$

The Slater determinant is also agreeable with the requirement that no two electrons in an atom or molecule have the same quantum numbers. As if two rows or columns of a determinant are identical, the determinant will be equal to zero, which then there is no system under the study.

5.8. HARTREE THEORY FOR MULTI-ELECTRON ATOMS

The bottleneck of quantum mechanical treatment of multi-electron systems is the Coulombic repulsion terms, between electrons in the Hamiltonian operator. In 1927, Hartree formulated what is now known as the self-consistent field (SCF) method for overcoming the problem of calculation of the wavefunctions of many-electron atoms. The main principle of the Hartree approximate method for overcoming the problem of repulsion term, is the independency of an electron, as each particle or electron is considered independent, and assumed to be in the different orbital. He assumed that each electron moves in the spherically symmetrical potential that resulted from the combination of the force from the nucleus and the force from all the other electrons. According to this theory, the wave function of the system (Φ) can be expressed as a product of wavefunctions of electrons, as shown in this equation:

$$\Phi(r_1, r_2, r_3, \dots, r_n) = \phi_1(r_1) \cdot \phi_2(r_2) \cdot \phi_3(r_3) \dots \phi_n(r_n) \quad (5-64)$$

where $\varphi_n(r_n)$ is the wavefunction that corresponding to nth electron and nth orbital at a distance of r_n . Similarly, the Hamiltonian operator of the multi-electron system ($\hat{H}_{atom}$) can be expressed as the sum of Hamiltonians of constituents:

$$\hat{H}_{atom} = \hat{H}_{(1)} + \hat{H}_{(2)} + \hat{H}_{(3)} + \cdots + \hat{H}_{(n)} \quad (5-65)$$

On the other side, in this theory, the approximate effective potential covers the field due to the nucleus and all electrons, except the specified electron that is expressed as an average function ($U_{(i)}^*$). Therefore, the Hamiltonian operator for the individual electron (ith electron) can be presented as:

$$\hat{H}_{(i)} = \frac{-1}{2m_e} \nabla_{(i)}^2 + U_{(i)}^* \quad (5-66)$$

The approximate effective potential estimated by a linear combination of atomic orbitals, throughout eliminating the electron-electron interaction. Finally, according to the theory of Hartree, the Schrodinger equation for the ith electron can be expressed as:

$$\hat{H}_{(i)}\Psi_{(i)} = E_{(i)}\Psi_{(i)} \quad (5-67)$$

5.8.1. Hartree-Fock Method for Multi-Electron Atoms

In 1930, Fock developed the Hartree method through the addition of spin wavefunctions and Slater determinant, for determining the anti-symmetrical wavefunction. Such essential development that was added by Fock, is referred to as the Hartree-Fock SCF method. It should be noted that this method was developed for treating molecules by the addition of a term, nucleus-nucleus interaction.

5.9. EXERCISES

1. What is the fundamental principle of (a) variation theory, (b) perturbation theory?
2. What is the reason for using approximate methods in quantum mechanics?
3. D-lines do not exist in the line spectrum of hydrogen, helium, and neon, but they are found in several metals such as mercury? Why?
4. Is the Pauli principle called an exclusion principle? Why?
5. The energy level of the singlet state is higher than that of the triplet. Why?
6. Write the Slater determinant for nitrogen atom.
7. What is the main principle of the Hartree theory?
8. What are the main differences between Hartree and Hartree-Fock methods?
9. State the reason for selecting the variational variable (ω) in treating the helium atom, using variational theory.

Chapter 6

APPROXIMATE SOLUTIONS OF THE SCHRÖDINGER EQUATION IN MOLECULAR SYSTEMS

6.1. INTRODUCTION

The treatment of molecules, using quantum mechanics is quite more tedious than that of atoms. It is simply due to the presence of at least two nuclei, which must be taken into consideration. In other words, there is a nucleus-nucleus interaction in addition to the interaction between electrons. There are three methods for treating the electronic structure of molecules. The most common are those of both valence bond theory (VBT) and molecular orbital theory (MOT). While the third one is the density functional theory (DFT), which has been renewed recently.

6.2. BORN-OPPENHEIMER APPROXIMATION

The electrons are responsible for the chemical reactivity of molecules in contrast to nuclei. Moreover, the electrons are moving faster than

nuclei. The speed of the electron is about 10^8 cm.s^{-1} within the atom or molecule, whereas for a nucleus is about 10^5 cm.s^{-1} , which is about 1000 times slower than that for electrons. Therefore in 1927, Born and Oppenheimer suggested that the nuclei of the molecule could be considered as fixed. Mathematically, this approximation plays an important consequence in solving molecules, as allowing the drop of the nuclear kinetic energies (Laplacian operator) of nuclei from the Hamiltonian operator of molecules.

6.3. VALENCE BOND THEORY (VBT)

This theory states that the bonding between atoms can be occurred by sharing the unpaired valence electrons when their molecular orbitals are overlapped. Atoms with no unpaired valence electron, such as He cannot make such bond, whereas atom with more than one unpaired valence electron could make multiple bonds, such as N_2 molecule (triple bond).

In 1927, Heitler and London used the VBT for solving hydrogen molecules as the following:



The wave function Ψ can be represented by this equation:

$$\Psi = 1s_A(1).1s_B(2) \quad (6-1)$$

where $1s_A$ and $1s_B$ presenting the $1s$ orbitals of atoms A and B for their electrons (1) and (2). However, Eq. (6-1) is not acceptable from a distinguishability point of view, according to the uncertainty principle.

In order to overcome this problem, one could write the following wavefunction ($\Psi^\#$):

$$\Psi^\# = 1s_A(2).1s_B(1) \quad (6-2)$$

Thus, two correct equations can be obtained by the summation and subtraction of Eqs. (6-1) and (6-2), as follows. Noting that the Pauli exclusion principle is not valid for molecules.

$$\Psi^+ = (\Psi + \Psi^\#) = 1s_A(1).1s_B(2) + 1s_A(2).1s_B(1) \quad (6-3)$$

$$\Psi^- = (\Psi - \Psi^\#) = 1s_A(1).1s_B(2) - 1s_A(2).1s_B(1) \quad (6-4)$$

The average or expectation values of these wave functions (Ψ^+ and Ψ^-) can be written, according to postulate IV.

$$E^+ = \frac{\int \Psi^+ \hat{H} \Psi^+ d\tau}{\int \Psi^+ \Psi^+ d\tau} \quad (6-5)$$

$$E^- = \frac{\int \Psi^- \hat{H} \Psi^- d\tau}{\int \Psi^- \Psi^- d\tau} \quad (6-6)$$

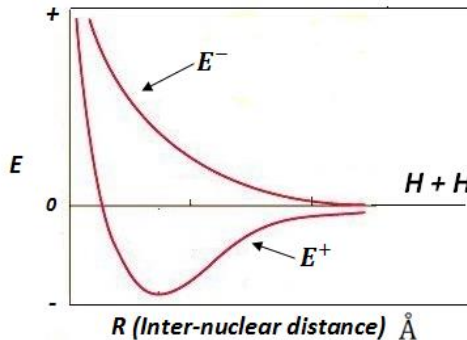


Figure 6-1. The schematic presentation of the energies (E^+ and E^-) that belong to Ψ^+ and Ψ^- against inter-nuclear distance (R) of H_2 , using VBT.

Figure 6-1 shows schematically the energies (E^+ and E^-) that belong to Ψ^+ and Ψ^- against inter-nuclear distance (R). The symmetrical wavefunction (Ψ^+) represents the hydrogen molecule as having the lowest energy in contrast to that of Ψ^- .

The relationships of Figure 6-1 can be explained at Ψ^- state, as there is no bonding between hydrogen atoms but only a repulsion, which decreases with an increase in the distance until the atoms are completely separated. In other words, the atoms prefer to be single as energetically favored. On the other hand, there is a substantial decrease in E^+ , until reaching the minimum, which represents the bond length. The first decrease could be attributed to the decreases in the electrostatic repulsion between the nucleus until the energy reaches the zero value, indicating the balance between repulsion and attraction forces. Then, the repulsion force is vanishing until reaches the high stability at the minimum value of energy. Subsequently, the energy increases due to the attraction force between atoms until the atoms are separated completely due to bond breaking. Moreover, at E^+ the valence bond between hydrogen atoms can be formed when the spin of electrons are paired or in the singlet state, as explained schematically in Figure 6-2. While at E^- , there is no bonding due to the repulsion between the valence electrons, which resulted from the triplet state as described in Figure 6-3. Finally, one could conclude that the covalent bond is formed by a magnetic force in contrast to others, which are due to electrostatic forces.

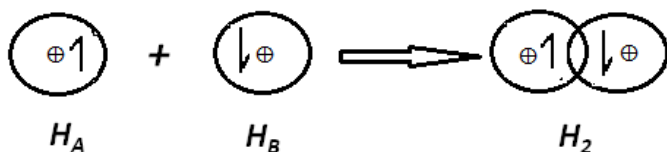


Figure 6-2. The schematic presentation of the singlet state of E^+ .

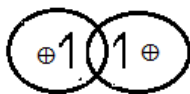


Figure 6-3. The schematic presentation of the triplet state of E^- .

6.4. MOLECULAR ORBITAL THEORY (MOT)

This method is differing from VBT, as there is no need for the bonded electrons to be localized between the two atoms in a molecule. In general, the treatment of systems by MOT is quite complex, compared to the VBT, as will be started by the ion of a hydrogen molecule.

6.4.1. The Hydrogen Molecule Ion (H_2^+)

The hydrogen molecule ion can be represented by the following (Figure 6-4):

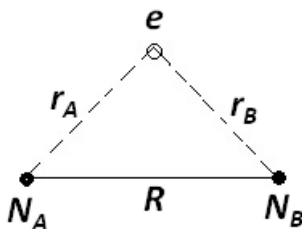


Figure 6-4. The hydrogen molecule ion H_2^+ .

According to the Born-Oppenheimer approximation, the Hamiltonian operator of hydrogen molecule ion can be written as:

$$\hat{H} = \frac{-\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R} \quad (6-7)$$

The wavefunction (Ψ) for this molecule can be expressed in terms of the linear combination of atomic orbitals:

$$\Psi = C_A \phi_A + C_B \phi_B \quad (6-8)$$

where the coefficients C_A and C_B are atomic parameters for A and B atoms, whereas ϕ_A and ϕ_B are $1s$ orbital functions of A and B atoms, respectively.

Using the variation principle, one could write the following secular determinant for H_2^+ :

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{vmatrix} = 0 \quad (6-9)$$

where $H_{AA} = \int \phi_A \hat{H} \phi_A d\tau$, $H_{AB} = \int \phi_A \hat{H} \phi_B d\tau$, $H_{BB} = \int \phi_B \hat{H} \phi_B d\tau$, $H_{BA} = \int \phi_B \hat{H} \phi_A d\tau$, and $S = \int \phi_A \phi_B d\tau$. S represents the overlap integral between A and B atoms, which is equal to S_{AB} and S_{BA} . H_{AA} and H_{BB} are representing the energy of an electron in the field of A and B atoms, respectively. H_{AB} or H_{BA} are representing the energy of an electron in the field between A and B nuclei. Noting that S_{AA} and S_{BB} are both equal to unity due to normalization ($S_{AA} = \int \phi_A \phi_A d\tau = 1$).

If one supposes that $H_{AA} = H_{BB}$ and $H_{AB} = H_{BA}$ as the atoms are identical, therefore, the secular determinant of Eq. (6-9) will be as the following:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{AA} - E \end{vmatrix} = 0 \quad (6-10)$$

The solution to this secular determinant is:

$$(H_{AA} - E)^2 - (H_{AB} - ES)^2 = 0 \quad (6-11)$$

solution The algebraic of the last equation gives a quadratic equation (second-order polynomial with 3 coefficients), which can be solved by quadratic formula ($x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$), in order to give two values of energy (E_1 and E_2). For mathematical purposes, the solution of the quadratic equation gives real and fictional values, which the later must be eliminated. Here, we have two equations of energy, one positive as E_1 and the other is negative as E_2 , and one of them is representing the molecule.

$$E_1 = \frac{H_{AA} + H_{AB}}{1 + S} \quad (6-12)$$

$$E_2 = \frac{H_{AA} - H_{AB}}{1 - S} \quad (6-13)$$

On the other hand, the secular equations of Eq. (6-9) will be used for evaluating the corresponding wavefunctions of E_1 and E_2 via multiplying by the coefficients C_A and C_B , as represented in Eqs. (6-14) and (6-15).

$$C_A(H_{AA} - E) + C_B(H_{AB} - ES) = 0 \quad (6-14)$$

$$C_A(H_{AB} - ES) + C_B(H_{BB} - E) = 0 \quad (6-15)$$

Substituting E_1 from Eq. (6-12) to E in Eq. (6-14), one could get:

$$C_A = C_B \quad (6-16)$$

Similarly, substituting E_2 from Eq. (6-13) to E in Eq. (6-15) gives:

$$C_A = -C_B \quad (6-17)$$

Ψ_1 could be described by the normalization of the molecular orbital of Eq. (6-8), as the following:

$$\int (C_A \phi_A + C_B \phi_B)^2 d\tau = 1 \quad (6-18)$$

which could give:

$$\int C_A^2 \phi_A^2 d\tau + \int 2C_A C_B \phi_A \phi_B d\tau + \int C_B^2 \phi_B^2 d\tau = 1 \quad (6-19)$$

The normalization of the wavefunctions ϕ_A and ϕ_B leads to:

$$C_A^2 + 2C_A C_B S + C_B^2 = 1 \quad (6-20)$$

where S is equal to $\int \phi_A \phi_B d\tau$.

Substituting Eq. (6-17) into the last Eq. (6-20) gives,

$$2C_A^2 + 2C_A^2 S = 1 \quad (6-21)$$

$$\therefore C_A = \pm \frac{1}{\sqrt{2+2S}} \quad (6-22)$$

Then, substituting the positive value of C_A from Eq. (6-22) to Eq. (6-8) gives Ψ_1 as follows:

$$\Psi_1 = \frac{1}{\sqrt{2+2S}} (\phi_A + \phi_B) \quad (6-23)$$

Similarly, one could get Ψ_2 by substituting Eq. (6-17) into the following equation:

$$\int (C_A \phi_A - C_B \phi_B)^2 d\tau = 1 \quad (6-24)$$

for obtaining Ψ_2 as follows:

$$\Psi_2 = \frac{1}{\sqrt{2-2S}} (\phi_A - \phi_B) \quad (6-25)$$

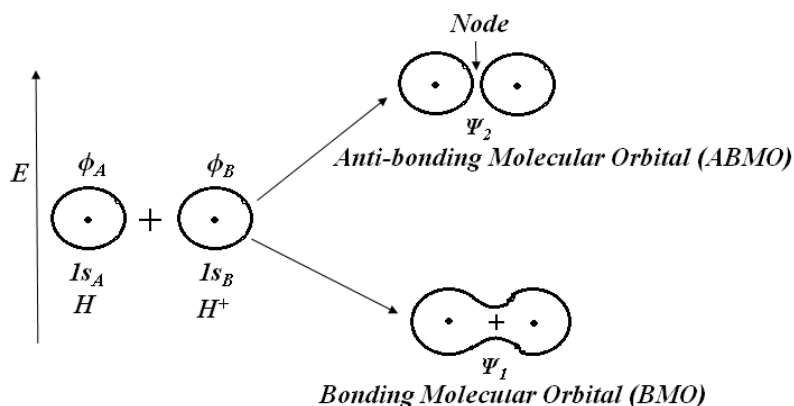


Figure 6-5. Ψ_1 acts as bonding molecular orbital and Ψ_2 functions as anti-bonding molecular orbital for hydrogen molecule ion H_2^+ .

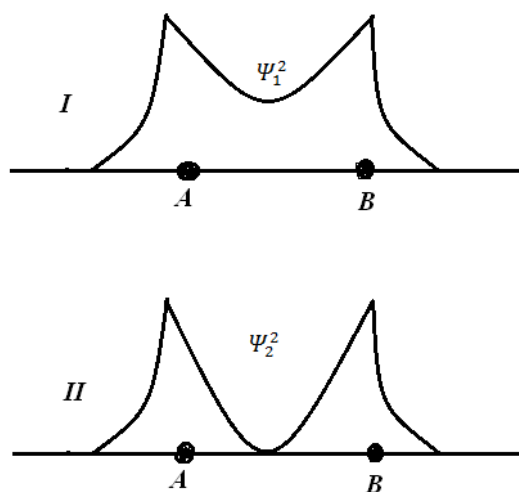


Figure 6-6. Probability densities of (I) Ψ_1^2 and (II) Ψ_2^2 along with the internuclear axis of hydrogen molecule ion H_2^+ .

It is found that E_1 and Ψ_1 represent the hydrogen molecule ion, as there is a bonding between hydrogen atoms, leading to loss of energy and a more stable state. In contrast, E_2 and Ψ_2 do not represent the molecule, which functions as anti-bonding, as illustrated below in Figure 6-5. Figure 6-6 explains in terms of probability density that at Ψ_1^2 , there is a

probability of finding the electron between the two nuclei, but for Ψ_2^2 , never one could find any electron.

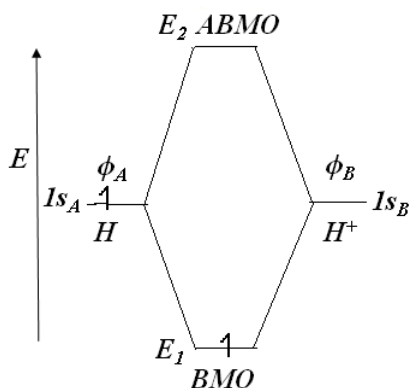


Figure 6-7. The energy level diagram for hydrogen molecule ion H_2^+ .

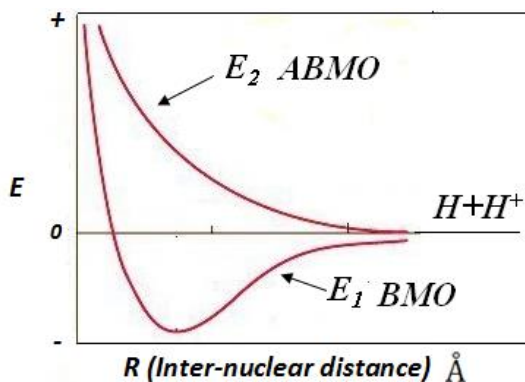


Figure 6-8. The schematic presentation of the energies (E_1 and E_2) against inter-nuclear distance (R) of hydrogen molecule ion H_2^+ , using MOT.

The relative energies of the two molecular orbitals are shown in Figure 6-7. E_1 is the lowest energy of the bonding molecular orbital (BMO), whereas E_2 is the highest energy of the anti-bonding molecular orbital (ABMO). The relationship between the energies versus internuclear distance (R), is described schematically in Figure 6-8. The relationship is quite similar to that of previous VBT for E^+ and E^- . At the

E_2 state, the hydrogen molecule ion is unstable and dissociates spontaneously to $H^+ + H$ while releasing energy.

6.4.2. The Hydrogen Molecule (H_2)

The H_2 molecule can be represented by Figure 6-9, in order to evaluate its Hamiltonian operator, as given in Eq. (6-26).

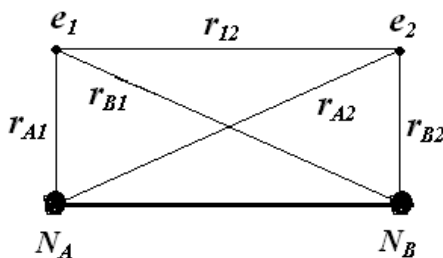


Figure 6-9. Hydrogen molecule H_2 .

$$\hat{H} = \left(\frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B1}} \right) + \left(\frac{-\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B2}} \right) + \frac{e^2}{r_{12}} + \frac{e^2}{R} \quad (6-26)$$

If one neglect the electron-electron repulsion term (e^2/r_{12}) of Eq. (6-26), approximately it will be the sum of two Hamiltonian operators of hydrogen molecule ion. Thus, the Hamiltonian operator of the hydrogen molecule can be rewritten as:

$$\hat{H} = \hat{H}(1) + \hat{H}(2) \quad (6-27)$$

Substituting the last equation into the Schrödinger equation gives:

$$(\hat{H}(1) + \hat{H}(2))\Psi = E\Psi \quad (6-28)$$

According to the previous hydrogen molecule ion problem, ψ_1 represents the molecular orbital of this molecule (BMO). Therefore, Ψ for hydrogen molecule can be represented as follows:

$$\Psi = \psi_1(1) \cdot \psi_1(2) \quad (6-29)$$

The complete wavefunction that includes the electron spin can be determined, using the Pauli exclusion principle, like the following:

$$\Psi = \psi_1(1) \cdot \psi_1(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (6-30)$$

or even by using the Slater determinant:

$$\Psi = \psi_1(1) \cdot \psi_1(2) \frac{1}{\sqrt{2}} \begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix} \quad (6-31)$$

6.5. HÜCKEL MOLECULAR ORBITAL THEORY (HMOT)

This method is adopted for treating conjugated hydrocarbons, in order to approximately estimate their electronic structures. Such type of hydrocarbon is containing two kinds of bonding electrons σ and π . However, there are only σ electrons in saturated hydrocarbons. The increase in chemical reactivity of conjugated hydrocarbons, in contrast to those of saturated, is attributed to the presence of π electrons. Therefore, Hückel proposed that σ electrons can be considered as fixed. For example, ethylene is the simplest conjugated hydrocarbon, containing 12 bonding electrons, including 10 of σ type and 2 of π type, however, only 2 π electrons will be taken into account, while disregarding the other 10 σ electrons (Figure 6-10).

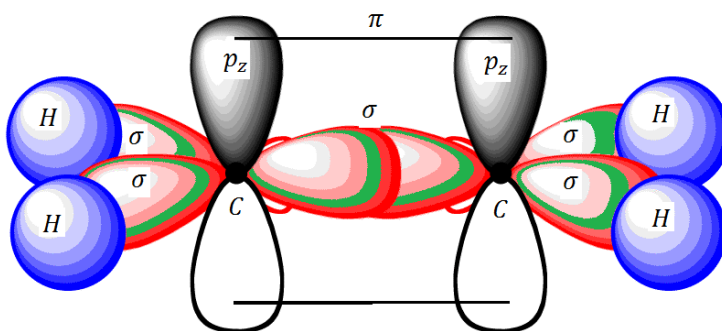


Figure 6-10. Ethylene molecule $\text{CH}_2 = \text{CH}_2$.

In general, the Hückel method can be summarized by two main steps. Firstly, the wavefunction of π electrons can be estimated by the linear combination of atomic orbital (LCAO). Secondly, the eigenvalue of the system is estimated, using the variation principle, including some special postulates. The method can be illustrated for estimating the electronic structure of the ethylene molecule, like the following.

The wavefunction of π or P_z electrons (Ψ_π) for N carbon atoms can be expressed by the following general model:

$$\Psi_\pi = \sum_{i=1}^N a_i \phi_i \quad (6-32)$$

where ϕ_i is the P_z atomic orbital and a_i is its coefficient. Hence, for ethylene molecule can be rewritten as:

$$\Psi_\pi = a_1 \phi_1 + a_2 \phi_2 \quad (6-33)$$

The eigenvalue (E_π) is determined by the variation principle, using the following secular determinant:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (6-34)$$

Then, Hückel used the following approximate postulates for simplifying the determinant:

The coulomb integral for an electron of each carbon atom is defined as α . Hence,

$$H_{11} = H_{22} = \alpha \quad (6-35)$$

The resonance integral for two directly bonded carbon atoms is defined as β . Hence,

$$H_{12} = H_{21} = \beta \quad (6-36)$$

Noting that if the carbon atoms are not bonded directly, then the resonance integral will be equal to zero, as it will be seen in the forthcoming examples.

The P_z orbitals are orthonormal, therefore,

$$S_{11} = S_{22} = 1 \quad (6-37)$$

and

$$S_{12} = S_{21} = 0 \quad (6-38)$$

Substituting E by the energy of one P_z electron ϵ .

Thus, applying the above Hückel postulates to the secular determinant (6-34), one could get:

$$\begin{vmatrix} \alpha - \epsilon & \beta \\ \beta & \alpha - \epsilon \end{vmatrix} = 0 \quad (6-39)$$

Dividing the elements of this determinant by β gives:

$$\begin{vmatrix} \frac{\alpha-\epsilon}{\beta} & \frac{\beta}{\beta} \\ \frac{\beta}{\beta} & \frac{\alpha-\epsilon}{\beta} \end{vmatrix} = 0$$

Then,

$$\begin{vmatrix} \frac{\alpha-\epsilon}{\beta} & 1 \\ 1 & \frac{\alpha-\epsilon}{\beta} \end{vmatrix} = 0 \quad (6-40)$$

Suppose,

$$x = \frac{\alpha-\epsilon}{\beta} \quad (6-41)$$

Substituting x of Eq. (6-41) into Eq. (6-40) yields:

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad (6-42)$$

The solution of this square determinant can be carried out as the following $x^2 - 1 = 0$

$$\therefore \begin{matrix} x = 1 \\ x = -1 \end{matrix} \quad (6-43)$$

Now, replacing the smallest value of x ($x=-1$) from Eq. (6-43) into Eq. (6-41), in order to obtain ϵ_1 as follows:

$$\begin{aligned} -1 &= \frac{\alpha - \epsilon_1}{\beta} \\ -\beta &= \alpha - \epsilon_1 \\ \therefore \epsilon_1 &= \alpha + \beta \end{aligned} \quad (6-44)$$

Similarly, one could get ϵ_2 by replacing the larger value of x (Eq. (6-43)) in Eq. (6-41).

$$\epsilon_2 = \alpha - \beta \quad (6-45)$$

Then, the resulted ϵ_1 and ϵ_2 are placed in the fixed Hückel energy level diagram, as shown in Figure 6-11.

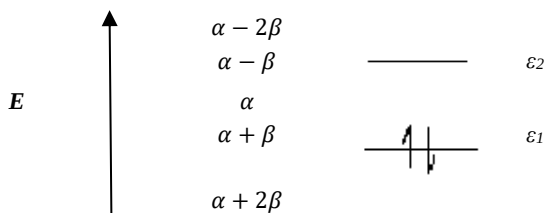


Figure 6-11. The energy level diagram for π electrons in the ethylene molecule.

Hence, the total energy (E_π) of ethylene is depending on the number and the level of electrons, which can be determined as the following:

$$E_\pi = 2\epsilon_1 = 2(\alpha + \beta) \quad (6-46)$$

$$\therefore E_\pi = 2\alpha + 2\beta \quad (6-47)$$

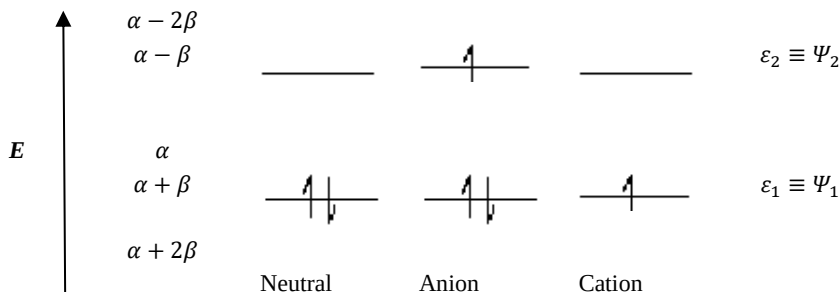


Figure 6-12. The energy level diagram for π electrons in the ethylene system.

Note: the total energy (E_π) for the ethylene system, including the anion and cation can be determined similar to ethylene molecule as only there is an addition in the energy level diagram (Figure 6-11), shown in Figure 6-12.

The eigenvalue for the anion and cation of ethylene can be estimated as the following:

$$E_\pi^- = 2\varepsilon_1 + \varepsilon_2 = 2(\alpha + \beta) + (\alpha - \beta) \quad (6-48)$$

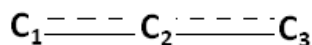
$$\therefore E_\pi^- = 3\alpha + \beta \quad (6-49)$$

$$E_\pi^+ = \varepsilon_1 = (\alpha + \beta) \quad (6-50)$$

$$\therefore E_\pi^+ = \alpha + \beta \quad (6-51)$$

where E_π^- and E_π^+ are the total energies for the anion and cation of ethylene molecule, respectively.

6.5.1. Example: Allyl Radical



$$\Psi_\pi = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 \quad (6-52)$$

The secular determinant for the eigenvalue (E_π) is:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{vmatrix} = 0 \quad (6-53)$$

$$H_{11} = H_{22} = H_{33} = \alpha \quad (6-54)$$

$$H_{12} = H_{21} = H_{23} = H_{32} = \beta \quad (6-55)$$

$$H_{13} = H_{31} = 0 \quad (6-56)$$

$$S_{11} = S_{22} = S_{33} = 1 \quad (6-57)$$

$$S_{12} = S_{21} = S_{23} = S_{32} = S_{13} = S_{31} = 0 \quad (6-58)$$

Substituting the Hückel postulates (Eqs. (6-54) to (6-58)) into Eq. (6-35) gives:

$$\begin{vmatrix} \alpha - \epsilon & \beta & 0 \\ \beta & \alpha - \epsilon & \beta \\ 0 & \beta & \alpha - \epsilon \end{vmatrix} = 0 \quad (6-59)$$

Dividing the elements of this determinant by β gives:

$$\begin{vmatrix} \frac{\alpha - \epsilon}{\beta} & 1 & 0 \\ 1 & \frac{\alpha - \epsilon}{\beta} & 1 \\ 0 & 1 & \frac{\alpha - \epsilon}{\beta} \end{vmatrix} = 0 \quad (6-60)$$

Substituting $x = \alpha - \epsilon / \beta$ gives:

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \quad (6-61)$$

The last determinant is not squared, and cannot be solved directly. It can be solved by a cofactor method. The solution to this determinant, using the cofactor method is as follows:

$$x^3 - 2x = 0 \quad (6-62)$$

$$x(x^2 - 2) = 0 \quad (6-63)$$

$$\therefore x = 0, x = \sqrt{2} \text{ and } x = -\sqrt{2}$$

when $x = -\sqrt{2}$,

$$\epsilon_1 = \alpha + \sqrt{2}\beta \quad (6-64)$$

when $x = 0$,

$$\epsilon_2 = \alpha \quad (6-65)$$

when $x = \sqrt{2}$,

$$\epsilon_3 = \alpha - \sqrt{2}\beta \quad (6-66)$$

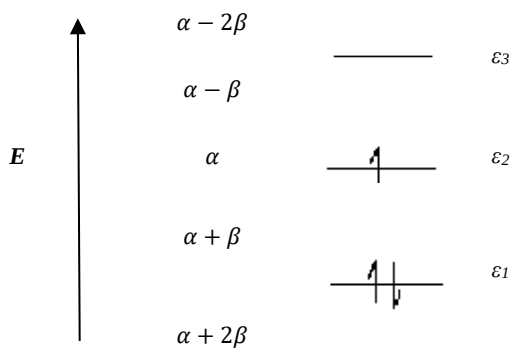


Figure 6-13. The energy level diagram for π electrons in allyl radicals.

$$E_{\pi} = 2\epsilon_1 + \epsilon_2 = 2(\alpha + \sqrt{2}\beta) + \alpha$$

$$\therefore E_{\pi} = 3\alpha + 2\sqrt{2}\beta \quad (6-67)$$

Hint: the cofactor method can be explained briefly as the following:

$$\begin{vmatrix} x_{11} & x_{12} & x_{13} \\ x_{21} & x_{22} & x_{23} \\ x_{31} & x_{32} & x_{33} \end{vmatrix} = 0$$

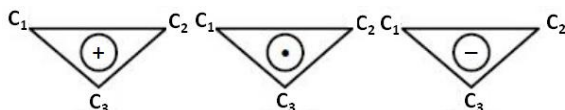
$$M_{11} = \begin{vmatrix} x_{22} & x_{23} \\ x_{32} & x_{33} \end{vmatrix}$$

$$M_{12} = \begin{vmatrix} x_{21} & x_{23} \\ x_{31} & x_{33} \end{vmatrix}$$

$$M_{13} = \begin{vmatrix} x_{21} & x_{22} \\ x_{31} & x_{32} \end{vmatrix}$$

$$x_{11}(-1)^{1+1}M_{11} + x_{12}(-1)^{1+2}M_{12} + x_{13}(-1)^{1+3}M_{13} = 0$$

6.5.2. Example: Cyclopropenyl System (Radical, Cation and Anion)



$$\Psi_{\pi} = a_1\phi_1 + a_2\phi_2 + a_3\phi_3$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} \end{vmatrix} = 0$$

$$H_{11} = H_{22} = H_{33} = \alpha$$

$$H_{12} = H_{21} = H_{23} = H_{32} = H_{13} = H_{31} = \beta$$

$$S_{11} = S_{22} = S_{33} = 1$$

$$S_{12} = S_{21} = S_{23} = S_{32} = S_{13} = S_{31} = 0$$

$$\begin{vmatrix} \alpha - \epsilon & \beta & \beta \\ \beta & \alpha - \epsilon & \beta \\ \beta & \beta & \alpha - \epsilon \end{vmatrix} = 0$$

$$\begin{vmatrix} \frac{\alpha - \epsilon}{\beta} & 1 & 1 \\ 1 & \frac{\alpha - \epsilon}{\beta} & 1 \\ 1 & 1 & \frac{\alpha - \epsilon}{\beta} \end{vmatrix} = 0$$

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

$$x(x^2 - 1) - 1(x - 1) + 1(1 - x) = 0$$

$$x^3 - x - x + 1 + 1 - x = 0$$

$$x^3 - 3x + 2 = 0$$

$$(x + 2)(x - 1)(x - 1) = 0$$

$$x = -2, x = 1 \text{ and } x = 1$$

Two similar values of x ($x=1$) indicate that there is a degeneracy.

when $x = -2$,

$$\epsilon_1 = \alpha + 2\beta$$

when $x = 1$,

$$\epsilon_2 = \alpha - \beta$$

when $x = 1$,

$$\epsilon_3 = \alpha - \beta$$

$$E_{\pi}^{+} = 2\varepsilon_1 = 2(\alpha + 2\beta) = 2\alpha + 4\beta$$

$$E_{\pi}^{-} = 2\varepsilon_1 + \varepsilon_2 = 2(\alpha + 2\beta) + (\alpha - \beta) = 3\alpha + 3\beta$$

$$E_{\pi}^{-} = 2\varepsilon_1 + 2\varepsilon_2 = 2(\alpha + 2\beta) + 2(\alpha - \beta) = 4\alpha + 2\beta$$

It should be noted that the solution of determinants can be obtained easily, using MATLAB, particularly for large conjugated molecules.

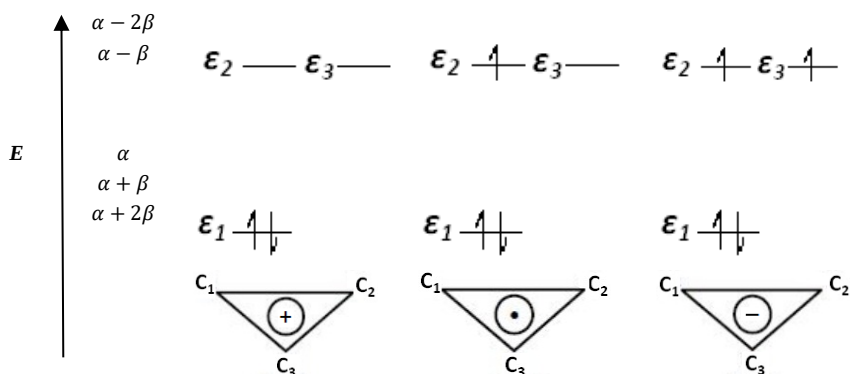
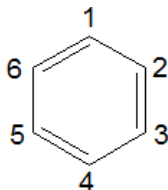


Figure 6-14. The energy level diagram for the cyclopropenyl system.

6.5.3. Example: Write the Secular Determinant of the Benzene Molecule, according to HMOT



$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix}$$

6.5.4. Determination of Coefficients

The coefficients of the wave function as a_1 and a_2 in Eq. (6-33) of ethylene can be determined as the following:

$$\Psi_{\pi} = a_1 \phi_1 + a_2 \phi_2 \quad (6-33)$$

$$\begin{vmatrix} a_1 \\ a_2 \end{vmatrix} \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (6-68)$$

Applying the Hückel postulates (Eqs. (6-35) to (6-38)) to the last determinant gives:

$$\begin{vmatrix} a_1 \\ a_2 \end{vmatrix} \begin{vmatrix} \alpha - \epsilon & \beta \\ \beta & \alpha - \epsilon \end{vmatrix} = 0 \quad (6-69)$$

Then, similar to the above for ethylene,

$$\begin{vmatrix} a_1 \\ a_2 \end{vmatrix} \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \quad (6-70)$$

$$\therefore \begin{matrix} x = 1 \\ x = -1 \end{matrix}$$

When $x = -1 \equiv \Psi_1 \equiv \varepsilon_1$

$$a_1 x + a_2 = 0 \quad (6-71)$$

$$a_1(-1) + a_2 = 0 \quad (6-72)$$

$$\therefore a_1 = a_2 \quad (6-73)$$

$$\text{Since } \sum_{i=1}^N a_i^2 = 1 \quad (6-74)$$

$$\text{For ethylene } a_1^2 + a_2^2 = 1 \quad (6-75)$$

Substituting a_2 of Eq. (6-73) into Eq. (6-75) gives:

$$\begin{aligned} a_1^2 + a_2^2 = 1 &\Rightarrow 2a_1^2 = 1 \\ a_1 &= \frac{1}{\sqrt{2}} \text{ and therefore } a_2 = \frac{1}{\sqrt{2}} \end{aligned} \quad (6-76)$$

$$\text{and } \Psi_1 = \frac{1}{\sqrt{2}} \phi_1 + \frac{1}{\sqrt{2}} \phi_2 \quad (6-77)$$

When $x = 1 \equiv \Psi_2 \equiv \varepsilon_2$, Eq. (6-71) becomes:

$$a_1(1) + a_2 = 0 \quad (6-77)$$

$$\therefore a_1 = -a_2 \quad (6-78)$$

According to Eq. (6-75)

$$a_1 = \frac{1}{\sqrt{2}} \text{ and then } a_2 = -\frac{1}{\sqrt{2}} \quad (6-79)$$

Hence,

$$\Psi_2 = \frac{1}{\sqrt{2}} \phi_1 - \frac{1}{\sqrt{2}} \phi_2 \quad (6-80)$$

$$\Psi_1 \equiv HOMO \text{ and } \Psi_2 \equiv LUMO$$

where *HOMO* is the highest occupied molecular orbital and *LUMO* is the lowest unoccupied molecular orbital. The band gap is the energy difference between *LUMO* and *HOMO*. In general, the energies of *HOMO* and *LUMO* are considered the most useful properties, as reflecting the activity of molecules.

6.6. EXERCISES

1. What is the suggestion of Born-Oppenheimer approximation and why?
2. Is there any important benefit that one could get by Born-Oppenheimer approximation from a mathematical point of view? Why?
3. Why the repulsion term in the relationship between energy and intermolecular distance of both VBT and MOT is considered as short-range, in contrast to that of attraction, which considered as long-range?
4. State the principle of Hückel molecular orbital theory (HMOT).
5. Why Hückel molecular orbital theory (HMOT) only applied to conjugated hydrocarbon systems?
6. *HOMO* and *LUMO* are called frontier orbitals? Why?
7. Write the secular determinant for butadiene, hexatriene, and anthracene.
8. Write the chemical structure of the compound that belongs to the following secular determinant:

$$\begin{vmatrix}
 x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 1 & x & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 1 & x & 0 & 0 & 0 & 0 & 0 & 1 \\
 0 & 0 & 0 & 0 & x & 1 & 0 & 0 & 0 & 1 \\
 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 & 0 \\
 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & x & 1 \\
 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 1 & x
 \end{vmatrix}$$

Chapter 7

INTRODUCTION TO COMPUTATIONAL CHEMISTRY

7.1. INTRODUCTION

The definition of computational chemistry is still controversial. Commonly computational chemistry is defined as “a branch of chemistry that uses computer simulation for solving chemical problems”. In other words, the term computational chemistry can be used for employing computer software for solving chemical problems. This means that computational chemistry is not captured by quantum mechanical calculations, in contrast to the field of theoretical chemistry. On the other side, computational chemistry could also be defined as a branch of chemistry that uses quantum mechanical calculations for solving chemical problems, which reflect in the syllabus that is taken by most scientific academies. This means that the establishment of computational chemistry is due to the presence of theoretical calculations based on quantum mechanics. In another word, computational chemistry can simply be defined as a branch of chemistry that employs computers, in order to determine very important information, usable for chemists and

physicists such as electronic structure, geometry optimization, bond length, angles, and many other useful properties. It is not surprising to say that any new empirical phenomenon that appeared in the literature could not become a fact until it is confirmed in terms of theoretical chemistry.

In general, the most important computational chemistry methods for molecular modeling can be divided into two main categories of molecular and quantum mechanics. Then, quantum mechanics can be divided into three subcategories: semi-empirical methods, *ab initio* methods, and DFT, as demonstrated in Figure 7-1.

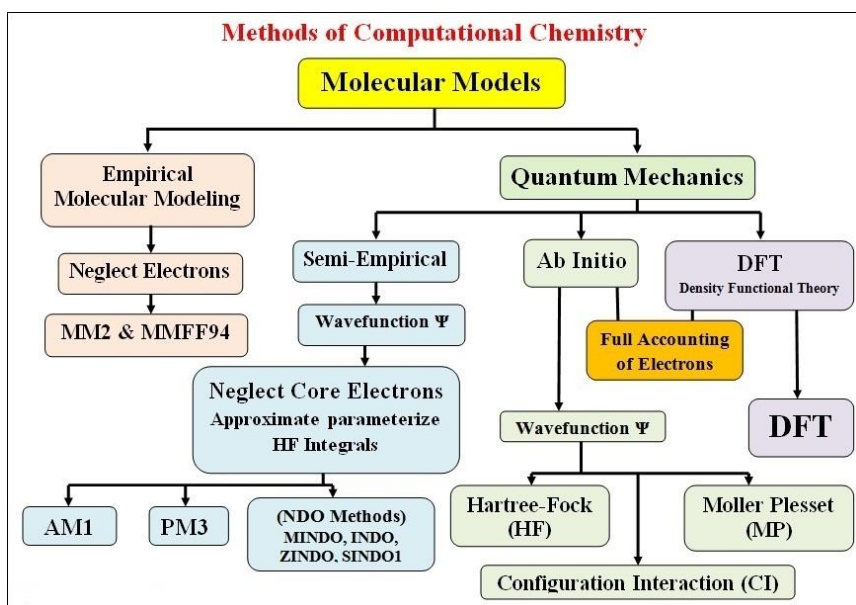


Figure 7-1. Methods of computational chemistry.

7.2. MOLECULAR MECHANICAL CALCULATIONS

This method applies the laws of classical physics to molecular nuclei, but only disregards the effect of electrons on the system, as the atoms are

considered as a ball at the end of spring. The main use of molecular mechanics is in the field of molecular dynamics. The basic idea of molecular dynamics is that the energy minimization could allow determining the forces, experienced by any atom with respect to other atoms. The steric energy is also employed in the minimization or optimization process. The total energy is the sum of force field contributions, depending on the degree of freedom, as illustrated in the coming equation. Furthermore, applying classical mechanics, including Newton's and Hook's laws in order to know how those forces would affect the motions of the atoms. The characteristic feature of molecular mechanics methods is that it can calculate any molecule with no regard to the number of atoms. The most common methods are MM2 (molecular mechanics 2) and MMFF94, which was developed by Merck pharmaceuticals.

$$E^{total} = \sum_i^{bonds} E_i^{stretch} + \sum_i^{bond\ angles} E_i^{bend} \\ + \sum_i^{dihedral\ angles} E_i^{stretch} + \sum_i \sum_j^{nonbonded\ atoms} E_{ij}^{nonbonded}$$

7.3. QUANTUM MECHANICAL CALCULATIONS

Quantum mechanics is considered a significant part of computational chemistry, which comparatively depends on the Schrödinger equation for describing the whole system, including nuclei and electrons. The methods of quantum mechanical calculations have three main categories, including semi-empirical, *ab initio* and DFT, as described briefly below.

7.3.1. Semi-Empirical Methods

Semi-empirical calculations are depending on the database of some experimentally measured properties. In other words, these methods are derived from the combination of experimental data and *ab initio* calculation, in order to simplify the difficulty of mathematical equations. The roots of the methods lie in the theory of π electrons, now extended to all-valence electron theories. For example, we can state extended Hückel method, Self-Consistent Field (SCF), and Hartree-Fock method (SCF-HF), such as CNDO (Complete Neglect of Differential Overlap), MINDO (Modified Intermediate Neglect of Differential Overlap), ZINDO (Zerner's Intermediate Neglect of Differential Overlap), PM3 (Parameterized Model number 3), AM1 (Austin Model 1) and so on. Semi-empirical methods can somewhat comparatively calculate large molecules of up to 100 atoms.

7.3.2. *Ab initio* Methods

Ab initio means from the beginning, which its calculations are based on the same principles of that of semi-empirical. In *ab initio* methods, the calculations of molecular orbitals only used the mathematical approximations, as there is neither experimental data nor neglecting of differential overlaps, like in the semi-empirical method. In this method, the calculations are covering the full accounting of electrons. Therefore, the calculations will be more complicated and time- consuming, in contrast to that of semi-empirical methods. As the calculations are depending on the number of electrons, the problem cannot be solved directly without using the iterative methods, such as the self-consistent field method. For example, HF (Hartree-Fock methods), MP (Moller Plesset), CI (Configuration Interaction), MCSCF (Multi-configuration Self-Consistent Field), CC (Coupled-Cluster), and so on. *Ab initio*

methods are considered as a computational expense, in which their calculations are limited to small molecules that cannot reach or exceed 50 atoms.

7.3.3. Density Functional Theory (DFT)

The term functional is differing merely from the related function, as it means the function of a function. For example, for function $f(x) = x^2$ then $f(2) = 4$, but for functional $F[f] = \int_0^1 f(x)dx$, then $F[x^2] = 1/3$. DFT is the newer method, which has some similarities with the last *ab initio* methods. The main difference is that in DFT, the energy of the system depends on its density rather than on the wave function, as in both *ab initio* and semi-empirical methods. In particular, HF potential of *ab initio* calculations was replaced by an exchange-correlation potential, which is a functional of the electron density. The exchange-correlation potential is including the effects of electron correlation, and hence can be more accurate than that of *ab initio* HF calculations, as shown by the models below. In more detail, in the DFT method, the wave functions of 3N spatial coordinates and N-spin coordinates are replaced by functional, belonging to electron density. Consequently, the computational expense of related *ab initio* methods is due to the fourth power scale (N^4) of the number of atomic orbitals. In addition, the last power scales, creating considerable numerical errors that have a bad effect on the accuracy of calculations.

$$E^{HF} = E^{nuclear} + E^{core} + E^{Coulomb} + E^{exchange}$$

$$E^{DFT} = E^{nuclear} + E^{core} + E^{Coulomb} + E^X(n) + E^C(n)$$

where $E^X(n)$ is the exchange functional and $E^C(n)$ is the correlation of functional, which are both added to the HF calculations.

The most advantage of the DFT method is the increase in computational accuracy without the additional increase in computing time. DFT is now considered the most successful approach for computing the electronic structure of even large molecules, in addition to the prediction of a variety of important molecular properties.

7.4. EQUILIBRIUM MOLECULAR STRUCTURE

The term “chemical structure” has been mentioned in 1861 by Butlerov. Chemical structure, also called molecular structure is considered as the most essential parameter for reflecting the basic information about the molecule, including both physical and chemical properties. On the other side, there is a problem arisen from the elucidation of molecular structure from different sources, which cannot give always the same results. Therefore, the equilibrium of molecular structure should be carried out by a combination of experimental results with quantum mechanical computations. In other words, the equilibrium molecular structure is a molecular structure that elucidated from the balance between experimental results with quantum mechanical methods.

7.5. ENERGY MINIMIZATION

As we have mentioned previously in the variation principle (Section 5.2), the calculated energy is mostly more than the real energy of the system. Thus, the energy minimization, also called energy or geometry optimization, is a basic process for reaching the lowest structure or conformation energy, by changing the bond lengths and angles in order to reduce the steric energy or inter-atomic forces. For example, the energy minimization of a water molecule is carried out by optimizing its

geometry throughout minimizing the forces of pulling the atoms together or pushing them apart by changing bond lengths and H-O-H bond angle.

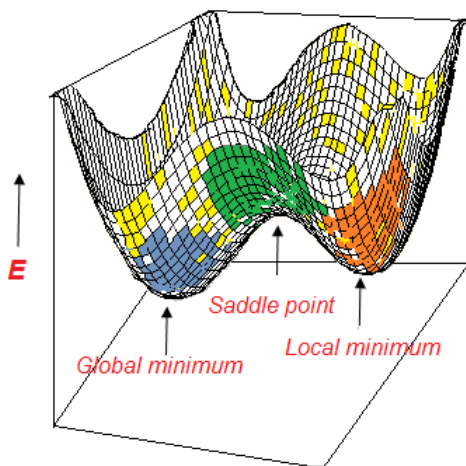
For estimation of the properties of any molecule, the minimization process must be already done and continued until reaching the global minimum. It should be noted that there is only one global minimum throughout arranging the geometry of particle atoms, in contrast to that of local minima for studying the transition state of chemical reactions. Furthermore, the local minimum can be detected from the potential energy structure as will be discussed in the proceeding section. In general, the global minimum can be reached systematically from light to heavy theoretical methods as starting from molecular mechanics, followed by semi-empirical and *ab initio* or DFT, including small to large basis sets.

7.6. POTENTIAL ENERGY SURFACE

The term potential energy diagram or curve is used in chemical kinetics for elucidating the reaction pathway concerning the activation energy. In computational chemistry, the applied term is potential energy surface (PES), a schematic tool that belongs to energy minimization for describing a molecule, set of molecules, a molecule of different conformations, or a probable system of a chemical reaction. The PES can be considered as a fingerprint for each molecule. Thus, different molecule gives different PES except that there is a different PES for the same molecule at the ground and excited states.

In general, the PES is represented by a multi-dimensional surface as dimensionally increases, with increasing the number of independent variables of atoms. It is well-known that each atom has three independent variables *x*, *y*, and *z* coordinates, and it is quite difficult or even impossible to show a surface of the many-atoms model. Hence, introducing two coordinates such as *x* and *y* for an atom should be

sufficient for establishing the potential energy surface, as shown in Figure 7-2. The main interesting regions that one could find from the topography of PES are extrema, as indicated by arrows in Figure 7-2. The extremum of lowest energy, called the global minimum, belongs to the most stable conformation. Only one global minimum could be found for the molecule, in contrast to the related local minima, as arisen from additional low energy extrema. In general, the term minima can be explained as a region of potential energy surface that yields higher energy geometry in any direction. The extremum area between two low energies is called a saddle point. The saddle points are quite helpful for determining the chemical structure of the transition state. Furthermore, there are what so-called orders of the saddle, such as first-order, second-order saddle point, and so on, as depending on the direction of the minimum. From a mathematical point of view, the extrema can be detected from the slope between energy and coordinate, when it is equal to zero ($\frac{\partial E}{\partial q} = 0$, where q is any coordinate).



Scheme 7-2. The potential energy surface.

7.7. EXERCISES

1. What are the main differences between molecular and quantum mechanics?
2. What are the main difference between computational chemistry and theoretical chemistry?
3. What is the advantage of the DFT method?
4. Which methods of computational chemistry take the wavefunction Ψ into account?
5. Which method of computational chemistry can be employed for the calculation of supramolecules?
6. What is the main practical problem, using *ab initio* method?
7. Which method of computational chemistry is more expensive from a computational point of view?
8. What is the more precise method for molecular modeling?
9. What is the advantage of the saddle point of the potential energy surface?
10. What is the value of the slope that belongs to the extrema of potential energy surface?

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