COURSE GUIDE

CHM 307
ATOMIC AND MOLECULAR STRUCTURE AND SYMMETRY

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INTRODUCTIONS

Theories of molecular structure can be generally divided into classical and quantum theories. The classical theory considers atom as a particle in having a well-defined geometric in space, while quantum theory attempts to explain molecular structure on the bases of the Schrodinger equation. The oldest of these theories is the classical theory, which was able to propose that all atoms have electron that revolves in an orbit, having a characteristic levels and energy. Several scientists were deeply involved in researches concerning the true picture of atom and its elemental particles. However, there are several properties of molecules or compounds that the classical theories cannot explain. For example, the concept of spin angular momentum and other intrinsic properties. Since atom consists of elementary particles whose size and dimension are very small, then the use of quantum theories along with classical theories provides a better objective to study molecular structure and symmetry. This indicates that concepts such as orbital properties, angular momentum, spin, coupling, bonding and anti-bonding molecular orbitals and other are subjects of atomic and molecular structure.

COURSE COMPETENCIES

Atomic and molecular symmetry (CHM 307) is a three credits unit course designed to cover the following concepts: Schrödinger equation. Helium atom, ground and excited states, spin and Pauli principles, hydrogen molecule, comparison of molecular orbital and Valence bond theories; concepts of resonance and configuration of orbital for historic molecular, Walsh rules. Rotational and vibrational bond length and angles. Brief mention of other methods, atomic spectra, Russell Sounder's coupling, orbital and spin angular momentum. Use of symmetry in chemistry. Heat capacities of solids. Theory of bonding in hydrogen molecular ion and hydrogen atom. Rotation and vibration of molecules. Heat capacities of crystals. This textbook arranged the topics into six different groups, identified as studied section.

This course is aimed to bring the student to the knowledge of fundamental aspects of atomic and molecular symmetry including derivation of Schrodinger equation, application of Schrodinger equation to orbitals, solving orbitals problems, particle in a one-dimensional box, etc. Molecular spectroscopy theories are also considered including, vibrational, rotational, electronic and rovibrational spectroscopies. The concept of coupling, resonance and Wlsh's rule are also considered. Considerations and discussions are also presented for symmetry and group theory, with special references to symmetry element, symmetry point group, classification of point group and application of symmetry.

The book is concluded by discussion of heat capacity of crystal solid. Several laws associated with heat capacity are derived and explained in study section 6. These included Dulong and Petite law, Francis Lois law and the Einstein law.

COURSE OBJECTIVES

When you have studied this course, you should be able to:

i. Understand the Schrodinger equation, its derivation from first principle and application in solving molecular structure problems.
ii. know how to apply the Schrödinger equation to find solution to some problems including a particle in a one dimensional box, hydrogen molecular ion problem, hydrogen and helium atoms problems
iii. understand the concept of spin, angular momentum and coupling (spin-spin coupling, Russell-Saunders coupling and JJ coupling)
iv. know the concept of molecular spectroscopic with detail discussion of dipole requirements for spectroscopic transition (vibrational, rotational, electronic and rovibrational spectroscopies)
v. explain the Walsh's rule, Walsh's diagram and their application
vi. explain the concept of resonance
vii. explore the significant of Dulong and Petite as well as Einstein laws in calculating the heat capacity of solid crystal
viii. bring the student to the understanding of the meaning of symmetry, group theory, symmetry elements and their application to molecular problems.
ix. explain the concept of bonding in molecules using hybridization, the valence bond and molecular orbital theories

WORKING THROUGH THIS COURSE

The course is structured into five models. Modules 1 to 3 consist of two units each while modules 4 and 5 consist of one unit each. It is necessary that for the student to study and understand the content of all the units in the respective modules.

You will be provided with the following materials:

1. Course Guide
2. Study Units

STUDY UNITS

The course is divided into three modules. Each module consist of two units as shown below

Module 1

Study Unit 1: The Schrödinger equation
Study Unit 2: Theories of bonding

Module 2

Study Unit 1: Molecular Spectroscopy
Study Unit 2: Coupling in Spectroscopy

Module 3

Study Unit 1: Symmetry and Group Theory
Study Unit 2: Heat capacity of solid Crystal

Study unit 1 (in module 1) introduces the Schrodinger equation and derived the equation from first principle. The components of the equation (including orbitals, wave function, Hamiltonianm) are highlighted and discussed. The use of the Schrodinger equation in solving some quantum chemical and structural problems are also discussed in study section 1. Symmetric/anti-symmetric wave functions, Pauli's exclusion principle are also discussed in study section 1

In study unit 2 (in module 1), theories of bonding are introduced. The valence bond theory and molecular theory are discussed in derail. The concept of hybridization, types of hybridization and solving problems related to hybridization are also discussed in this study section. Hydrogen molecular ion, hydrogen and helium atoms' problem are solved using the Schrodinger equation.

In module 2 study unit 1, molecular spectroscopy is introduced with special reference to vibrational, rotational, rovibration and electronic spectroscopy. The use of simple harmonic oscillator and Hooke's models in explaining vibrational and rotational spectroscopy have been deeply treated;

In study unit 2 of module 2, the concept of coupling with special reference to spin-orbit, Russell-Sanuders and JJ coupling,

In study unit 1 of module 3, symmetry and group theory are discussed with special reference to symmetry group, group theory, symmetry elements, symmetry operations and application of symmetry.

Finally, in study unit 2, heat capacity is defined. Models (Dulong and Petite, Loius and Einstein) explaining heat capacity of solid crystal are also discussed in detail.

REFERENCES AND FURTHER READNGS

Textbooks referred to in the development of each units are presented at the end of the units. However, list of some General references are presented below:

Allinger, N. L (2010). *Molecular structure: Understanding steric and electronic effects from molecular mechanics*. John Willey and Son, USA Aruldhas (2007). *Molecular structure and spectroscopy*. Prentice Ha;; of India

Atkins, P. and De Paula, J. (2010). *Atkins'Physical chemistry*. 9th Edition. Oxford University Press. UK.

Banwell, C. N. (1983), Fundamental of molecular spectroscopy, McGraw-Hill International. UK

Demaison, J., Boggs, J. E. and Csaazar, A. G. (2010). *Equilibrium molecular structures*. CRC press. Taylor and Francis group, UK

Dhaduk, B. (2019). *A textbook of physical Chemistry*. Lambert Publishing, UK

Engel T. and Reid, P. (2005). *Physical chemistry*. Pearson Cummings. San Francisco. New York.

Hofmann, A. (2018). *Physical Chemistry essentials*. Springer International Publishing. Switzerland

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Lagana, A and Parker, G. A. (2018). *Chemical reactions*. Springer International Publishing. Switzerland

Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

Struve, W. S. (1989). *Fundamental of molecular spectroscopy*. John
        Willey and Sons. New York

Struvel, W. S. (1987), *Fundamental of molecular spectroscopy* Springer
        International Publishing. Switzerland

Tamvakis, K. (2019). *Basic quantum mechanics*. Springer International
        Publishing. Switzerland AG

Telxeira-Dias, J. J. C. (2017). *Molecular physical chemistry*. Springer
        International Publishing, Switzerland.

PRESENTATION SCHEDULE

This course is presented in three different modules. Each module
consists of two study units. Each module begins with introduction, study
outcomes and main content. Within the main content, fundamental facts
are presented along with inline worked examples and answers. Each unit
ends with summary, conclusion, bibliography, self assessment
questions/answers and activity for student to test their comprehension.

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked
assignment (TMA) and end of course examination. The TMAs shall
constitute the continuous assessment component of the course. They will
be marked by the tutor and equally account for 30 % of the total course
score. Each learner shall be examined in four TMAs before the end of
course examination. The end of course examination shall constitute 70%
of the total course score.

HOW TO GET THE MOST FROM THE COURSE

Student are expected to comprehends best information out of this course
through careful study of each units. It is recommended that student
should test their ability to answer questions that follow each unit as well
as questions in reference materials related to this course.

MAIN COURSE

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MODULE 1

UNIT 1 THE SCHRODINGER EQUATION

1.0   INTRODUCTION

Atom consists of proton, electron and neutron. The proton is positively charged and is about 1836 times heavier than the negatively charged electron. Neutron, which was discovered in 1932 has no charge and is slightly heavier than the proton. The first set of investigation on the structure of atom started between 1908 and 1913, when Rutherford, Hans Geiger and Ernest Marsden repeatedly passed a beam of alpha particle through a thin metal foil in the Physical Laboratories of the University of Manchester and observed the deflection of the particle through a fluorescence screen. In their experiment, they discovered that most of the alpha particle passed through the foil undeflected, few were strongly deflected and others were deflected backward. From the findings of their experiment, they noted that such large deflection is possible if the positive charge was concentrated in a tiny heavy nucleus and concluded that every atom contains a nucleus where its positive charge and most of its mass are concentrated. In 1904, J. J. Thompson had suggested that the positive charges were spread throughout the atom but Rutherford and co-workers refuted this fact on the grounds that if it were so, then once the high energy atom penetrates the atoms, the repulsive forces would have fallen off and eventually become zero.

Nowadays, it is known that atom contain Z number of proton and number of Z electrons (where Z is the atomic number). The mass of the

atom is concentrated in the central nucleus (which contains proton and neutron, collectively called nucleons). The nucleus is held together by strong nuclear forces while the nucleus and the electrons are held together by columbic force of attraction. In 1911, Rutherford proposed the planetary model of the atom, which stated that electron revolves around the nucleus. However, this model was exposed to several criticism. Classically, electromagnetic theory expects an accelerating ally charge particle to radiate electromagnetic waves. Also, a rotating charge radiating electromagnetic waves with changing velocity and direction will gradually lose energy and the atom will be unstable and eventually collapse.

In 1913, Niels Bohr offered explanation to the Rutherford theory through the concept of quantization of energy in the hydrogen atom. Bohr stated the energy of electron in hydrogen is quantized with electron allowed to move only in a number of allowed circle.

Bohr found that when hydrogen gas is heated, it emits electromagnetic radiation, characterised by certain distinct frequencies. Such spectral frequencies were explained according to equation 1.1

$$\frac{v}{c} = \frac{1}{\lambda} = \left(\frac{1}{n_b^2} - \frac{1}{n_a^2}\right) \qquad \qquad 1.1$$

where $n_b = 1, 2, 3 \dots, n_a = 2, 3 \dots n_a > n_b$ and R is the Rydberg constant $= 1.096776 \times 10^5 cm^{-1}$

Classically, all frequencies of light ought to have been emitted but this is not true hence Einstein equation implies that the hydrogen atom exist in certain energy states. Indeed, an atom can has only certain energies, E_1, E_2, E_3 .... These allowed states of constant energy are called the stationary states. An atom in a stationary state can only emit radiation when its makes transition from a stationary state of higher level to the stationary states of lower energy and will therefore satisfied equations 2.2 and 2.3;

$$E_{Higher} - E_{Lower} - h\nu \qquad \qquad 1.2$$
$$E_a - E_b = h\nu \qquad \qquad 1.3$$

Combination of equations 2.1 and 2.3, yields equation 1.4

$$E_a - E_b = Rhc\left(\frac{1}{n_b^2} - \frac{1}{n_a^2}\right) \qquad \qquad 1.4$$

The implication of equation 8 is that the energies of the H-atom stationary states can be written as

$$E = -\frac{Rhc}{n^2} \qquad \qquad 1.5$$

The major limitation of the Bohr theory arises from the use of classical mechanics to describe the motion of an electron in an atom. Evidence obtained from spectra of atoms reveals discrete frequencies which indicates that only certain energies of motion is allowed and that the electronic energy is quantized. Classically, continuous range of energies are possible but quantum mechanically, the energy is restricted to certain permissible values.

Although Bohr model was satisfactory in explaining the hydrogen atom, it fails to explain poly electron systems. In order to extend quantization to systems with two or more electrons, Louis de Broglie in 1923 found that just as light shows both wave and particle aspect, matter also has a dual nature, as well as showing particle like behaviour, electron could also show wave like behaviour, which manifest itself in the quantized energy levels of electrons in atoms and molecules. For photons, we have, $E_{photon} = h\nu$. Einstein special theory of relativity gives the energy of a photon as $E_{photon} = Pc$, where P is the momentum of the photon and c is the speed of light. Equating the two equations, we have $h\nu = pc$ and since $\nu = \dfrac{c}{h}$, we have

$$\frac{hc}{\lambda} = pc \ \text{ or } \ \lambda = \frac{hc}{p} = \frac{h}{mv}$$

      1.6

In 1927, the German physicist, Werner Heisenberg stated that the more precise the position of some particle is determine, the less precisely the momentum can be known and vice versa. However,, Earle Hesse Kennard and Hermann Wey in 1928 were able to derived the formal inequality that relates the standard deviation of position, a_x and that of momentum a_p as follows,

$$a_x . a_p \geq \frac{\hbar}{2} \qquad\qquad\qquad\qquad\qquad\qquad 1.7$$

In quantum mechanics, uncertainty principle is any of the variety mathematical inequalities that sustain a fundamental limit to the precision with which certain pairs of complementary physical properties can be known. Uncertainty principle is inherent in the properties of all wave like systems and it originate from the de Broglie wave matter duality principle. In quantum chemistry, the uncertainty principle is mostly use to explore the relationship between simultaneous measurement of position and momentum. Therefore, the principle can be restated as, the product of the uncertainties in position and in momentum is in the order of magnitude of Planck constant or greater i.e.

$$\Delta x . \Delta p \geq \frac{\hbar}{2} \qquad\qquad\qquad\qquad\qquad\qquad 1.8$$

where $\hbar$ is the reduced Planck constant. $\hbar = \dfrac{h}{2\pi}$

2.0`   INTENDED LEARNING OUTCOMES (ILOS)

When you have studied this session, you should be able to:

* Comprehends developmental stages of quantum chemistry and associated models such as Einstein, Bohr, Planck, etc.
* Know how to derive time independent Schrödinger equation from first principles
* Interpret the various components of the Schrödinger equation (Wave function, operator, eigen value, etc) and their physical significant.
* Apply the theory of Schrödinger to the concept of orbital
* Answer questions related to the Schrödinger equation
* Understand the concept of orthogonality
* Understand how to use Schrodinger equation to find solution to a particle in a one-dimensional box
* Understand the concept of symmetric and anti-symmetry
* Understand Pauli's exclusion principles
* Be able to solve quantitative and qualitative problems associated with the Schrodinger equation

3.0   MAIN CONTENT

3.1   The time independent Schrödinger equation

The Schrödinger equation is like the Newton' s law and the law of conservation of energy in classical physics because it aids in predicting the future behaviour of dynamic system. This work of Schrödinger was initiated by Einstein in 1925, when he published a paper on quantum theory of ideal gas, and the de Broglie theory of matter waves. However, in 1926 Erwin Schrödinger proposed an equation that describes the evolution of a quantum mechanical system è SWE which represents quantum equations of motion in the following forms:

$$\frac{-\hbar \partial^2 \psi}{2m\partial x^2} + V(x)\,\psi(x,t) = i\hbar\frac{\partial \psi}{dt}$$
$$\left[\frac{-\hbar \partial^2}{2m\partial x^2} + V(x)\right]\psi(x,t) = i\hbar\frac{\partial \psi}{dt}$$

This is an equation that describes how the quantum state of a system changes with time. We can derive, the Schrödinger equation using the unique equation,

$$\Psi = A\frac{\sin 2\pi x}{\lambda} \qquad\qquad 1.9$$

Differentiating equation 1.10 with respect to x, we have;

$$\frac{d\Psi}{dx} = \frac{2\pi}{\lambda}A\cos\frac{2\pi x}{\lambda} \qquad\qquad 1.10$$

Taking a second derivative of equation 13 with respect to x yields equation 1.11;

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}A\sin\frac{2\pi x}{\lambda} \qquad\qquad 1.11$$

Since $\psi = \frac{\sin 2\pi x}{\lambda}$, equation 2.11 can be simplified to the form given by equation 1.12

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi \qquad\qquad 1.12$$

Equation 1.12 can be simplified by applying the de Broglie equation, which relates particle momentum to wavelength as, $\lambda = \frac{h}{mv}$. Therefore, $\lambda^2 = \frac{h^2}{m^2v^2}$ and substituting for λ^2 in equation 1.12, equation 1.13 is obtained

$$\frac{d^2\varphi}{dx^2} = \frac{4\pi^2}{\left(\frac{h^2}{m^2.v^2}\right)}\psi = \frac{-4m^2v^2\pi^2}{h^2}\psi \qquad\qquad 1.13$$

The total energy of a system is the sum of the kinetic energy (KE = ½ mv²) and the potential energy (U), i. e. E = KE + U = ½ mv² + U and v² = 2/m (E – U). Modification of equation 2.13 through substituting the value of v² by 2/m (E – U) leads to equation 2.14

$$\frac{d^2\varphi}{dx^2} = \frac{-8m\pi^2}{h^2}(E-U)\psi \qquad\qquad 1.14$$

Introducing the reduced Planck constant, = h/2 , equation 2.14 becomes,

$$\frac{d^2\varphi}{dx^2} = \frac{-2m}{\hbar^2}(E-U)\psi$$
$$1.15$$

Equations 2.14 and 2.15 are the various differential forms of the time independent Schrödinger equation for a one-dimensional system. For a three-dimensional system, the following equations are obtained,

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2} = \frac{-8m\pi^2}{h^2}(E-u)\varphi$$
$$1.16$$
$$= (\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2})\psi = \frac{-8m\pi^2}{h^2}(E-u)\psi$$
$$1.17$$
$$= \nabla^2 = \frac{-8m\pi^2}{h^2}(E-u)\psi \qquad\qquad 1.18$$

$$= \nabla^2 \quad = \frac{-2m}{\hbar^2}(E-u)\psi \qquad\qquad 1.19$$

where ∇^2 is called Laplacian operator, $\nabla = \frac{\partial}{dx} + \frac{\partial}{dy} + \frac{\partial}{dz}$. The Schrödinger equation can be re-arranged by collecting like terms as follows,

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi = E\psi \quad \text{or} \quad \left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + U\right)\psi = E\psi$$
$$1.20$$

The first term $\left(\frac{-h^2}{2m}\frac{\partial^2}{dx^2} + U\right)$ is called the Hamiltonian operator, which operates on ѡ to give the energy E and the wave function. Therefore, the general form of the Schrödinger equation can be written as   = E . The Schrödinger equation is on eigen equation or eigen function of the form (operator) (function) = (numerical value) x (function). The numerical function in this case is the energy and is called an eigen value. Solving the Schrödinger equation involves finding the value of the eigen value. The importance of eigen value equation is that it is consistent with the following patterns,

(Energy operator) (wave function) = (Energy) (wave function)
(operator) (wave function) = (observable) (wave function)

From the above, if we know both   and the operator corresponding to the observable of interest, we can predict the outcome of an observation of that property.

3.1.1 The wave functions

The Schrödinger equation is the fundamental equation in quantum mechanics. The wave function does not have any physical significant but the square of the wave function represents the probability density of finding a system in a given time. This assertion was proposed by Max Born. Max, also proposed four conditions that must be fulfilled when the solution to the Schrödinger equation is sought for. Born's conditions to be imposed on the wave function, ψ are:

i.   The wave function must be single valued. This means that for any given values of x and t ψ, must have a unique value. This is a way of guaranteeing that there is only a single value for the probability of the system being in a given state. Actually, if ψ is a proper mathematical function, it will satisfy this requirement automatically, since one condition all functions must satisfy is that they are single-valued.

ii.   The wave function must be quadratically integratable. This implies that, the integral of $|\psi|^2$ over all space must be finite. This is another way of saying that it must be possible to use

$|\psi|^2$as a probability density, since any probability density must integrate over all space to give a value of 1, which is clearly not possible if the integral of $|\psi|^2$is infinite. One consequence of this proposal is that the wave function must tend to 0 for infinite distances.

iii.   The wave function must be continuous at all points, indicating that there should not be a sudden jump in the probability density when moving through space. If a function has a discontinuity such as a sharp step upwards or downwards, this can be seen as a limiting case of a very rapid change in the function. Such a rapid change would mean that the derivative of the function was very large (either a very large positive or negative number). In the limit of a step function, this would imply an infinite derivative. Since the momentum of the system is found using the momentum operator, which is a first order derivative, this would imply an infinite momentum, which is not possible in a physically realistic system.

iv.   All first-order derivatives of the wave function must be continuous. Following the same reasoning as in condition iii, a discontinuous first derivative would imply an infinite second derivative, and since the energy of the system is found using the second derivative, a discontinuous first derivative would imply an infinite energy, which is not physically realistic.

3.1.2 The Operator

An operator is an instruction, a symbol which tells us to perform one or more mathematical acts on a function, say *f(x)*. The essential point is that they act on a function. Operators act on everything to the right, unless the action is constrained by brackets.

i.   Addition and subtraction rule for operators:
$$(\hat{A}_1 \pm \hat{A}_2)f(x) = \hat{A}_1 f(x) \pm \hat{A}_2 f(x)$$
1.21

ii.   The product of two operators requires successive operation. For example,
$$\hat{A}_1.\hat{A}_2 f(x) = \hat{A}_1[\hat{A}_2.f(x))]$$ 1.22
It should be noted that the product of two operators is the third operator, i.e, $\hat{A}_3 = \hat{A}_1.\hat{A}_2$

iii.   Two operators are said to commute if the obey the simple operator expression
$$[\hat{A}_1.\hat{A}_2] = \hat{A}_1.\hat{A}_2 - \hat{A}_2.\hat{A}_1 = 0$$. This indicate that $\hat{A}_1.\hat{A}_2 = \hat{A}_2.\hat{A}_1$

The commutivity of two operators implies that the observables associated with these two operators can be measured simultaneously. This is contrary to the Heisenberg uncertainty principles which requires non commutivity. For example, the non-commutivity of the position and the momentum operators (the inability to simultaneously determine particles position and its momentum) is represented with the Heisenberg uncertainty principle as $\Delta x . \Delta p \geq \frac{h}{2} = \frac{1}{2} |\langle [\hat{x}, \hat{p}] \rangle|$.

3.1.3 Schrödinger equation and orbital

The solution of the Schrödinger equation involves finding the eigen value through the eigen function. Several wave functions such as ψ_1, ψ_2, ψ_3, ψ_4,….. may satisfy the requirements for the Schrödinger equation and each of them has corresponding eigen value such as the energy, E_1, E_2, E_3, E_4……. respectively. Each of this wave function is called an orbital and the square of each of them represent the probability of finding electron within a given volume element. For example, ψ_1 can be used to represent the ground state orbital of hydrogen atom because its single electron will first occupy the first orbital. The energy of this orbital will be E_1.

Each atom has a number of acceptable solutions to the Schrödinger wave equation and each orbital may be described by a set of three quantum numbers namely,

i.   The Principal quantum number, n: describes the energy level of electron
ii.   The subsidiary quantum number, l: describes the shape of orbital occupied by electrons. Values of l includes the integers and zero, i.e 0, 1, 2, 3, 4…. When $l = 0$, 1, 2 and 3, the orbitals are s-orbital, the p-orbital, the d-orbital and the f-orbital respectively. The letter s, p, d and f originate from spectroscopy and are sharp, principal, diffuse and fundamental respectively
iii.   The magnetic quantum number, m: describes the paramagnetic or diamagnetic properties of electron. When $l = 0$, m = 0

Based on allowed solutions to the Schrödinger equation, orbitals can generally be classified into three groups. These are

i.   Those whose probability of finding electrons is a function of distance, r from the nucleus and the probability, $|\psi|^2$ is the same in all direction. The s-orbital is the only orbital in this group
 ii.   Those whose wave function depends on the distant from the nucleus and on the direction in space (x, y, z). Orbitals in this group are characterised by subsidiary quantum number equal

to 1 and are called p-orbital. There are three possible values of the magnetic quantum number, i.e m = -1, 0, +1, indicating that there are three sub orbitals for orbital in this group. These are,

- $\psi_x = f(r). f(x)$
- $\psi_y = f(r). f(y)$
- $\psi_z = f(r). f(z)$

These sub orbitals have the same energy. Therefore, there are three degenerate orbitals for each of the value of n = 2, 3, 4

    iii.   The third group consist of orbitals whose wave function depends on distance from the nucleus, r and also on two directions in space. For example, the d and f orbitals. For the d-orbital, the subsidiary quantum number, is 2 and the magnetic quantum number, m = 4, i.e., -2, -1, 0, +1, +2. Therefore, there are four degenerate sub orbitals for the d-orbital formed when n = 3, 4, 5. These are,

    i. ψ_{x-y} = f(r). f(x). f(y)
    ii. ψ_{x-z} = f(r). f(x). f(z)
    iii. ψ_{y-z} = f(r). f(y). f(z)
    iv. ψ_{z^2} = f(r). f(z). f(z)
    v. $\psi_{z^2-y^2}$ = f(r). $f(z^2)$. $f(y^2)$

The subsidiary quantum number for the f-orbital, l is 3 indicating that the magnetic quantum number m = 7, i.e. -3, -2, -1, 0, +1, +2, +3. Therefore, there are seven degenerates sub orbitals for the f- orbital, which are formed when n = 4, 5, 6.

3.2   Orthogonality

If the wave function has different quantum numbers, then their overlap is zero and for two wave function, the overlap can be written as,

$$\int \psi_m \ddot{\psi}_n \, dx = \delta_{mn}$$

where δ_{mn} is called the Kronecker delta. It has the property such that $\delta_{mn} = 0$, if m = n and $\delta_{mn} = 1$, if m ≠ n.

3.3   Solution of the Schrödinger equation for a one electron system

Hydrogen atom, He^+ and Li^{2+} are example of a one electron system. The Schrödinger equation can be solved for these systems by converting the Cartesian coordinates (x, y, z) to the polar coordinates (p, θ, and φ). The coordinate of a point, P measured from the origin are x, y and z in

Cartesian coordinate and p, ϕ and θ respectively (See Fig 1.1). The relationship between Cartesian and polar coordinates are,
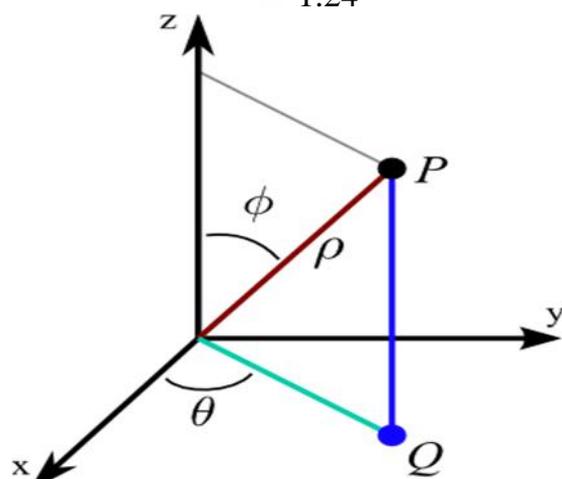
i. z = $p\cos\phi$
ii. y = $s\sin\phi\cos\theta$
iii. z − $s\sin\phi\cos\theta$

The three-dimension Schrödinger equation can be written as, ∇^2 + $\frac{8m\pi^2}{h^2}(E - u)\psi = 0$. where ∇ is the Laplacian operator, as defined before. Changing to polar coordinates, ∇^2 becomes,

$$\frac{1}{p}\cdot\frac{\partial}{\partial r}\left(p^2\frac{\partial\psi}{\partial p}\right) + \frac{1}{p^2\sin^2\phi}\cdot\frac{\partial^2\psi}{\partial\theta^2} + \frac{1}{p^2\sin\phi}\cdot\frac{\partial}{\partial\phi}\left(sin\phi\frac{\partial\psi}{\partial\phi}\right)$$
1.23

Without proof, the solution to equation 1.23 is in the form given by equation 1.24

iv. $\psi = R(p).\Phi(\phi).\Theta(\theta)$
1.24

**Fig. 1.1: Relationship between polar and Cartesian coordinates**

Equation 1.24 can be spitted into three components as follows,

i $R(p)$ is a function of the distance from the nucleus and depends on the quantum   number, n and l.
ii. $\Phi(\phi)$ is a function that depends on the quantum number, l and m
iii. $\Theta(\theta)$ is a function which depends only on m.
     From the above information, we can re-write equation 28 as follows,
$\psi = R(p)_{n,l} + P_{m,l}$
1.25

where $R(p)_{n,l}$ is the radial wave function which depends on the quantum number, n and l while $P_{m,l}$ is the total angular wave function which depend on the quantum number m and l. Although the radial function has no physical significant, the square of it, defines the probability of finding electron on a small volume element, dv. It has been found that for a given value of p, the number of small volumes is $4 p^2$. Therefore, the probability of an electron being at a distance p from the nucleus is $4 p^2.R^2$. This quantity is called the radial distribution function. Fig. 1.2 shows plots of radial distribution functions for various orbital. From the plots, it is evident that the probability is zero at the nucleus (i.e. $p = 0$) and for 1s, 2s and 3s, the most probable distance increases as the principal quantum number increases. If we compare the plots for 2s with that of 2p or 3s with that of 3p, it is evident that the most probable distance decreases with increase in the subsidiary quantum number.
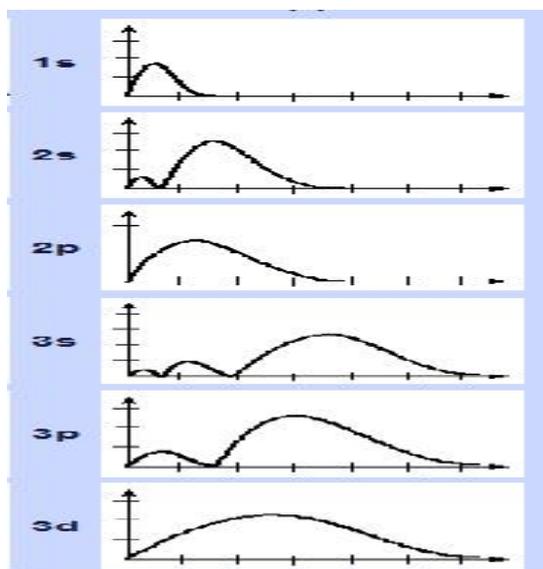
Fig. 1.2: Radial distribution functions for various orbitals

3.4 Symmetric/Antisymmetric Wave Functions

For a system of identical particles, which are indistinguishable from each other, interchanging the particles occupying any pair of states will not change the probability density, $|\psi|^2$ of the system. Let the particle wave function be ψ_{r_1,r_2} and ψ_{r_2,r_1}. The probability density of the two particles wave function will agree with the following expression

$$\left|\psi_{(r_1,r_2)}\right|^2 = \left|\psi_{(r_2,r_1)}\right|^2$$
    1.26

Equation 45 can be fulfilled under two major conditions. These are,

    (i)   symmetric case: $\psi_{(r_1,r_2)} = \psi_{(r_2,r_1)}$
    1.27

(ii)   Antisymmetric case:$\psi_{(r_1, r_2)} = -\psi_{(r_2, r_1)}$
                    1.28

From the above, it can be deduced that particles whose wave function are symmetric under particle interchange have integral or zero intrinsic spin (i,e, 0, 1, 2,3...) and are termed bosons. On the other hand, particles whose wave functions are anti-symmetric under particle interchange have half-integral intrinsic spin $\left(i.e \; \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, etc\right)$ and are termed

Fermions. Electrons are Fermions. Any number of bosons may occupy the same state but not two Fermions may occupy the same state.

Worked Example 1

Given a wave fonction, ψ = sinnx, find the solution to the Schrödinger équation,

Solution

The wave function Is defined as, ψ = sinnx. Operating ψ with $\hat{H}$, we have,

$$\hat{H}\psi = \frac{-\hbar^2}{2m} . \frac{d^2}{dx^2}(sinnx)$$
$$= \frac{n^2\hbar^2}{2m} . \frac{d^2}{dx^2}(sinnx)$$
$$\hat{H}\psi = \frac{n^2 h^2}{2m} . \frac{d^2}{dx^2}\psi \;(\text{note that } \psi = sinnx)$$

Worked Example 2

Show that $\psi = e^{-ax}$ are also an eigen function of $\hat{H} = -\frac{h^2}{2m} . \frac{d}{dx^2}$. Hence calculate the energy of the system if a = 2

Solution
Since $\psi = e^{-ax}$,

$$\frac{d\psi}{dx} = -ae^{-ax}$$
$$\frac{d^e\psi}{dx^2} = a^2e^{-ax}$$

Operating the given wave on the Hamiltonian operator, we have,

$$\hat{H}\psi = -\frac{\hbar^{2^2}}{2m} . \frac{d^2}{dx^2}(e^{-ax})$$

$$\hat{H}\psi = -\frac{\hbar^2}{2m}(a^2 e^{-ax})$$

$$\hat{H}\psi = -\frac{a^2\hbar^2}{2m}\psi$$

The general form of the Schrödinger equation is $\hat{H}\psi = E\psi$. Therefore, comparing this to the above expression, the energy of the system is E = $-\frac{a^2\hbar^2}{2m}$. Therefore, when a =2, the energy, E=$-\frac{2\hbar^2}{m}$

Worked example 3

Normalize the following wave function, $\psi = A\sin nx$, given that x lies in the range 0 to

Solution

The basic condition for a wave to be normalize is that, $\int \psi\psi^* \delta\tau = 1$. Since $\psi\psi^* = \psi^2$, then it can be stated that the given wave, $\psi = A\sin nx$, is normalize under the following condition,

$$\int \psi\psi^* dx = 1$$

$$\int_0^\pi (A\sin nx)^2 dx = 1$$

$$A^2 \int_0^\pi \sin^2 nx.\,dx = 1$$

The solution of the integral, $\int_0^\pi \sin^2 nx.\,dx$ is $\frac{\pi}{2}$. Therefore, for the normalization condition to be fulfilled, $A^2.\frac{\pi}{2}$ must be equal to unity.

That is $A^2.\frac{\pi}{2} = 1$, which gives $A = \sqrt{\frac{\pi}{2}}$. Hence the normalized wave function is $\sqrt{\frac{\pi}{2}}\,Sin(nx)$. $A = \sqrt{\frac{\pi}{2}}$ is called normalization factor.

Worked example 4

Under what conditions can you say that a wave function is orthogonal? Hence derive the orthogonal relationship for a particle in a one-dimension box.

Solution

If the wave function has different quantum numbers, then their overlap is zero and for two wave function, the overlap can be written as,

$$\int \psi_m \ddot{\psi}_n\, dx = \delta_{mn}$$

13

where δ_{mn} is called the Kronecker delta. It has the property such that $\delta_{mn} = 0$, if m = n and $\delta_{mn} = 1$, if m≠ n. let us write the orthogonality relationship for a particle in a one-dimensional box for example. The wave function for this particle is $j = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi}{a}\right) x$. If the there exist different quantum numbers, m and n, then, $\int \psi_m \dot{t}_n dx = \delta_{mn}$ and for the particle, we have,

$$\sqrt{\frac{2}{a}} \int sin\left(\frac{n\pi x}{a}\right) sin\left(\frac{m\pi x}{a}\right) dx$$

3.5   Pauli's Exclusion Principle

The fundamental idea behind the Pauli's exclusion principle is that no two electrons in an atom can have the same four quantum numbers (n, l, m and m_s). The theory considers symmetry and anti-symmetry properties of a complete wave function (which include spatial and spin coordinates) with respect to interchange of spatial and spin coordinates of any two particles.

Let us consider the wave function with respect to α and β electrons in helium, which can be written as,

$Œ = 1s\alpha(1)1s\beta(2)$
        1.27

Since electron is indistinguishable, the complete wave function can be written according to equation 1.28, which re-arrange to equation 1.29,

$Œ = 1s\alpha(1)1s\beta(2) + 1s\alpha(2)1s\beta(1)$
        1.28
$Œ = 1s(1)1s(2)[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$
        1.29

The requirements of equations 1.28 and 1.29 can also be met by the underlisted equations (equations 1.30 and 1.31)

$Œ = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$
        1.30
$Œ = 1s(1)1s(2)[(\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
        1.31

A close examination of equations 1.30 to 1.31 reveals that the wave function can be separated into spatial part $[1s(1)1s(2)]$ and the spin

part $([(\alpha(1)\beta(2) - \alpha(2)\beta(1)])$ or $[(\alpha(1)\beta(2) + \alpha(2)\beta(1)]$. The product of the orbital with the spin function is called spin orbital, Equation 1.29 is symmetry to electron interchange while equation 1.31 is anti-symmetry to electron interchange.

Pauli Exclusion Principle can be effectively analysed by considering a non-interacting qualifier for a two-particle wave function, which can be written as a product of two single particle wave function according to equations 1.32 and 1.33,

$$\psi_1(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) \qquad\qquad 1.32$$
$$\psi_{11}(r_1, r_2) = \psi_a(r_2)\psi_b(r_1)$$
$$\qquad 1.33$$

where a and b are two different single particle states. Since the particles are indistinguishable, the system can be considered as a combination of the two function, $\psi_1 and \psi_{11}$. Consequently, the only two correct normalized combinations that can be obtained are

(i)   Symmetric case:
$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[(\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1)] \ \ 1.34$$
(ii)   Anti-symmetric case:
$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}}[(\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)]$$
$$\qquad 1.35$$

In the case of fermions, if a = b, the   = o implying that no two Fermions can occupy the same state. This is the concept of Pauli exclusion principle and it is obeyed by Fermions and not by bosons. However, while fermions obey Femi-Dirac theory, bosons obey Bose-Einstein theory. Bosons systems therefore display outstanding properties, such as super-conductivity. Pauli exclusion principle can be re-stated as follows, the complete wave function for a system of identical fermions must be anti-symmetry with respect to interchange of all coordinate of any two particles. For a system of identical bosons, the complete wave function must be symmetry with respect to interchange of all coordinate of any two particle.

3.6   A Particle in a one-dimension Box

A particle in a 1-dimensional box is a fundamental quantum mechanical approximation describing the translational motion of a single particle confined inside an infinitely deep well without provision for it to escape. It is an application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem of a

particle in a one-dimensional box involves finding the possible values of the allowed energy, E and the wave function,   (x), whose square gives us the probability of locating the particle at a certain position within the box at a given energy level.

To solve the problem for a particle in a 1-dimensional box, the following steps are required,

i.   Defining the potential energy, V, within and outside the box
ii.   Solving the one-dimensional Schrödinger equation
iii.   Defining the wavefunction
iv.   Defining the allowed energies

Consider a particle in in a one-dimension box shown in Fig. 1.3. Three regions exist These are I, II and III. The particle can only move in region II and not I and III. This is a simple problem that is similar to an electron in atom considered to move within a distant x, which is between x = o and x = a. The potential energy is 0 inside the box (V=0 for 0<x<L) and goes to infinity at the walls of the box (V= for x<0 or x>L). It is assumed the walls have infinite potential energy to account for the fact that the particle has zero probability of being at the walls or outside the box.

The appropriate wave function for this system will be related to the Schrödinger equation for a one dimension according to equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \qquad\qquad 1.36$$

Since the potential energy V, is zero inside the box (i.e. location II) equation 1.36 becomes rearrange to 1.37 by putting V = 0:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi \qquad\qquad 1.37$$
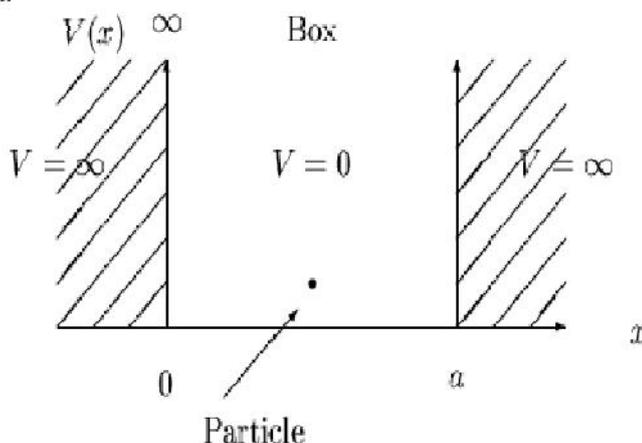
Fig.1.3: A particle in a one-dimension box

Solution of equation 1.37 is

$$\psi(x) = A\sin\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}x + B\cos\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}x$$
   1.38

Since the potential outside the box is zero, the probability of finding the particle must have a value of zero at these points. In order to satisfy the boundary conditions at x = 0, we have, $\psi(0) = A\sin(0) + B\cos(0) =$ Therefore, B = 0 and the second boundary condition implies that x = a. Hence,

$$\psi(a) = A\sin\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}a = 0 \qquad\qquad\qquad 1.39$$

The above equation is only true if $\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}a = n\pi$.where n is an integral (n = 1,2, 3,). ħ is the reduced Planck constant. = h/2π.

Substituting for $\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}a$ into equation 1.38, we have,

$$j = A\sin\left(\frac{n\pi}{a}\right)x \qquad\qquad\qquad 1.40$$

In order to calculate the value of A, it is assumed that the total probability of finding the particle inside the box is unity (1) indicating that there is no probability of the particle to be outside the box. This correspond to the wave function been normalized, i.e., $\int_0^a j^2 dx = 1$. Normalizing equation 1.40, equation 1.41 is obtained

$$A^2\int_0^a \sin^2\left(\frac{n\pi}{a}\right)xdx = 1$$
   1.41

From integral table, the solution to the above equation gives $A = \sqrt{\frac{2}{a}}$

and the normalised wave function is expressed in equation 1.42

$$,j = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}\right)x \qquad\qquad\qquad 1.43$$

Since$\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}a = n\pi$, it follows that$\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{a^2}$. Substituting for $\hbar^2 = \left(\frac{h}{2\pi}\right)^2 = \frac{h^2}{4\pi^2}$, we have equation 1.44, which simplified to equation 1.45 (that gives the expression for the allowed energy of a particle in a one dimension box

$$\frac{(2mE)x\ (4\pi^2)}{h^2} = \frac{n^2\pi^2}{a^2}$$
   1.44

$$E = \frac{n^2 h^2}{8mc^2} \qquad\qquad\qquad 1.45$$

where n = 1, 2, 3, 4 ………., From equation 69, a particle moving between two points in a line can have only the energies given by $E = \frac{n^2 h^2}{8ma^2}$. Such discrete energy levels are characteristic of solution of the Schrödinger equation for bound particles. No such energy level is expected on the basis of classical mechanics for example when n = 1, $E_1 = \frac{h^2}{8mc^2}$ indicating that a particle must have at least an energy value equal to $h^2/8ma^2$. It is only this value of E that makes the wave function, a well behave as a continuous function. The state of lowest energy for a quantum system is termed its ground state. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as zero-point energy. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. Confining the particle to be between 0 and 'a' implies that the wave function must be 0 at x = 0 and x= a. This also means that the energy is quantized. This can be compared to the vibration of a string fix at both ends. A zero- point energy is defined whenever a particle is constrained to a finite region otherwise, the uncertainty principle would have been violated. The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $P_{min} = \pm h/2a$. This can be expressed as an uncertainty in momentum given by p h/a. Coupling this with the uncertainty in position, x a, from the size of the box, we can write x p h, which agrees with the Heisenberg uncertainty principle

On the other hand, when n = 2, 3, 4, 5, we have

$$E = \frac{4h^2}{8ma^2} n = 2$$

$$E = \frac{9h^2}{8ma^2} n = 3$$

$$E = \frac{16h^2}{8ma^2} n = 4$$

From the above, it can be seen that the energy is restricted to a certain permissible value. For example, energies are multiple of 4, 9, 16 for n = 2, 3 and 4 respectively, hence the energy is quantised. The particle, therefore, always has a positive energy. This contrasts with classical systems, where the particle can have zero energy by resting motionlessly. This can be explained in terms of the uncertainty principle, which states that the product of the uncertainties in the position and momentum of a particle is limited by x P /2.It can be shown that the uncertainty in the position of the particle is proportional to the width of the box and that the uncertainty in momentum is roughly inversely proportional to the width of the box. The kinetic energy of a particle in a one dimension box is given as KE = $p^2/(2m)$ and hence the minimum kinetic energy of the particle in a box is inversely proportional

to the mass and the square of the well width.The wavefunction for a particle in a box at the n=1 and n=2 energy levels is shown in Fig. 1.4
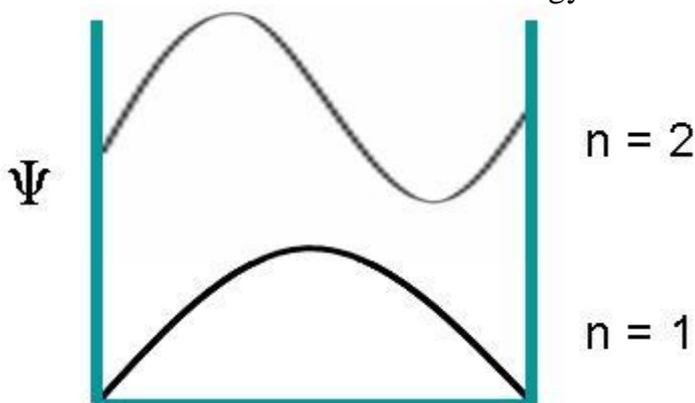
Fig. 1.4: Diagram showing the wave function for n = 1 and n = 2

The probability of finding a particle a certain spot in the box is determined by squaring the wave function. The probability distribution for a particle in a box at the n=1 and n=2 energy levels takes the pattern shown in Fig. 1.4. It can be seen from Fig. 1.5 that the number of nodes (places where the particle has zero probability of being located) increases with increasing energy n. Also, as the energy of the particle becomes greater, the quantum mechanical model breaks down as the energy levels get closer together and overlap, forming a continuum. This continuum means the particle is free and can have any energy value. At such high energies, the classical mechanical model is applied as the particle behaves more like a continuous wave. Therefore, the particle in a box problem is an example of wave particle duality.

Fig. 1.5: Diagram showing the variation of probability function for

n= 1 and n = 2 levels

4.0   (i)   Self-Assessments Exercise and Answers

1.   What is the major limitation of Bohr's model?

2.   Calculate the wave length of electron moving at 2 x 10^6m/s using the de Broglie equation

3.   Construct the Hamiltonian operator for a system whose energy is given as $E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V_{(x,y,z)}$

4.   if there are two particles in the system such that their masses are m_1 and m_2, construct the Hamiltonian for the system.

5.   What is spin orbital?

Answers to Self-Assessment Exercises

1.   The major limitation of the Bohr theory arises from the use of classical mechanics to describe the motion of an electron in an atom. Evidence obtained from spectra of atoms reveals discrete frequencies which indicates that only certain energies of motion is allowed and that the electronic energy is quantized. Classically, continuous range of energies are possible but quantum mechanically, the energy is restricted to certain permissible values.

2.   The Broglie equation gives the wave length of electromagnetic radiation, of which electron behaves in similar manner as , $\lambda = \frac{h}{mv}$ where m is the mass of electron. m = 9.1 x 10^{-3} kg. Therefore,

$$\lambda = \left(\frac{6.626 \times 10^{-34}}{(9.1 \times 10^{-3})\left(2 \times \frac{10m}{s}\right)}\right) = 3.6 \times 10^{-10}\text{m} =$$

$3.6A^o$

The result is in the order expected for elementary particles indicating that unique effect is important in electronic motions.

3.   We start by changing the classical momentum component to quantum mechanical operator, this

$$p_x \rightarrow \acute{P}_x = \frac{-i\hbar d}{dx}$$

$$p_y \rightarrow \acute{P}_y = \frac{-i\hbar d}{dy}$$

$p_z \rightarrow \acute{P}_2 = \frac{-i\hbar d}{d_z}$, Therefore;

$$p_x^2 \rightarrow \acute{P}_x^{\,2} = \left(\frac{-i\hbar d}{d_x}\right).\left(\frac{-i\hbar d}{d_x}\right) = \frac{-\hbar^2 d^2}{dx^2}$$

$$p_y^2 \rightarrow \acute{P}_y^2 = \left(\frac{-i\hbar d}{d_y}\right).\left(\frac{-i\hbar d}{d_y}\right) = \frac{-\hbar^2 d^2}{dy^2}$$

$$p_z^2 \rightarrow \acute{P}_z^2 = \left(\frac{-i\hbar d}{d_z}\right) \cdot \left(\frac{-i\hbar d}{d_z}\right) = \frac{-\hbar^2 d^2}{dz^2}$$

Therefore, the Hamiltonian operator can be written as;

$$\hat{H} = \frac{-1}{2m}\left(\frac{\hbar^2 d}{dx^2} + \frac{\hbar^2 d}{dy^2} + \frac{\hbar^2 d}{dx^2}\right) + V_{(x,y,z)}$$

$$= \frac{-\hbar^2}{2m}\left(\frac{d}{dx^2} + \frac{d}{dy^2} + \frac{d}{dx^2}\right) + V_{(x,y,z)}$$

$$= \frac{-\hbar^2}{2m}\nabla^2 + V_{(x,y,z)}$$

Where ∇ is the Laplacian operator, $\nabla = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$

4.   if there are two particles of masses, m_1 and m_2 and co-ordinate (x_1, y_1, z_1), $(,x_2, y_2, z_2)$, then the classical energy can be written as:

$$E = \frac{1}{2m_1}\left(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2\right) + \frac{1}{2m_2}\left(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2\right) + V_{(x_1,y_1,z_1,x_2,y_2,z_2)}$$

And   the   corresponding   Hamiltonian   is; $\hat{H} = \frac{-\hbar^2 \nabla_1^2}{2m_1} - \frac{\hbar^2 \nabla_2^2}{2m_2} +$

$V_{(x_1,y_1,z_1,x_2,y_2,z_2)}$

$$= \frac{-\hbar^2}{2}\left[\frac{1}{m_1}\nabla_1^2 + \frac{1}{r_2}\nabla_2^2\right] + V_{(x_1,y_1,z_1,x_2,y_2,z_2)}$$

5.   The product of the orbital with the spin function is called spin orbital

4.0   CONCLUSION

The fundamental wave equation is the Schrodinger equation and its importance is based on the fact that solutions to quantum systems can be derived through the Schrodinger equation. To a good extent, the Schrodinger equation has been used to explain several quantum system with good degree of certainty especially with the use of some computer softwares.

5.0   SUMMARY

The energy of a particle is quantized. This means it can only take on discreet energy values. The lowest possible energy for a particle is not zero (even at 0 K). This means the particle always has some kinetic energy. The square of the wavefunction is related to the probability of finding the particle in a specific position for a given energy level. The probability changes with increasing energy of the particle and depends on the position in the box we are attempting to define the energy. In

classical physics, the probability of finding the particle is independent of the energy and the same at all points in the box

6.0   TUTOR MARKED ASSIGNMENT

(1)   What are the major properties of a wave system:? (3 minutes)
(2)   What are the limitation of the Schrodinger equation in describing quantum systems (3 minutes)
(3)   Differentiate between time dependent and tine independent wave functions (5 minutes)

7.0   REFERENCES/FURTHER READINGS

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UNIT 2   THEORY OF BONDING

CONTENT

1.0   INTRODUCTION

There are two major approaches that can be used to calculate molecular structure. These are the valence bond theory (VBT) and the molecular orbital theory (MOT). VBT assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom and that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. The basis of VB theory is the Lewis concept of the electron pair bond. On the other hand, the MOT relies on the combination of atomic orbitals to form bonding and antibonding molecular orbitals. The former stabilizes the molecule while the latter destabilizes the molecule. However, these theories lack the capacity to explain the nature of bonding in some molecules, hence where the VBT fails, hybridization theory explain bonding in terms of promotion of electrons, the formation of hybrid orbitals before overlapping. Beyond the VBT, the MOT and hybridization, is the quantum mechanics, which has the potential of   explaining chemical bonding in most compounds

by considering the behaviour of electrons during bonding. Combination of all these theories are discussed in this study section

2.0   INTENDED LEARNING OUTCOME

When you have studied this session, you should be able to:

* Understand the valence bond theory of bonding in molecules and the conditions for overlap
* How atomic orbitals are mixed through hybridization in order to form bonding
* Know different types of hybridization and provide examples for each
* Know why resonance hybrid is needed to describe the chemical structure of some compounds and how to calculate resonance energy
* Understand the theory and application of Walsh's rule
* Understand the molecular orbital theory and their applications in explaining bonding in some compounds
* Differentiate between bonding molecular orbital and antibonding molecular orbitals
* Understand how pi and sigma bonds are formed
* Use the molecular orbital theory to calculate bond order and interpret magnetic property, stability and other properties of some compounds using bond order
* Understand theories of bonding in hydrogen molecular ion, helium and hydrogen atoms
* Be able to solve mathematical problems associated with theories of bonding

3.0   MAIN CONTENT

3.1   The Valence bond theory

The VBT considered that a bond is formed when an electron in an atomic orbital of one atom pairs its spin with that of an electron in atomic orbital of another atom. For example, in molecular hydrogen, the spatial wave functions for electron in each of the atom can be written as,

$$\Psi = \Psi_{(r_1)} \psi_{(r_2)} = \Psi(A)(1)\Psi(B)(2)$$
$$105$$

where A and B denotes the two atomic nuclei. In the case of hydrogen atom, the outcome of $\Psi(A)(1)$ and $\Psi(B)(2)$ are equally likely because the atoms are indistinguishable. The application of quantum mechanics requires that the total probability should be derived from superposition

of the wave function for each. Hence the valence bond wave function for hydrogen molecule can be written as, $Œ = Œ(A)(1)Œ(B)(2) + Œ(B)(1)Œ(A)(2)$.

The linear combination given by equation 106 will have an energy lower than that of any of the combining wave function because of constructive interference between $Œ(A)(1)Œ(B)(2)$ and $Œ(B)(1)Œ(A)(2)$. This implies that there will be an enhancement of the probability density of electron in the intermolecular region.

The valence bond theory relies on the overlap of orbitals of the combining atoms. Orbital overlap requires that the following conditions are met,

i.   Completely filled orbital cannot overlap. Consequently, only half filled orbital from one atom can combine with half-filled orbital from the other atom to form a new orbital, having opposite spin of electron

ii.   The atoms with bonding orbitals should be closely and properly align with the axis of their orbital

The strength of bond formed depends on the magnitude of the overlap, the greater the overlap, the greater the bond strength. Overlap orbital has energy lower than that of the isolated atoms, hence overlapping stabilises the compound. The stabilization energy (or bond energy) is the amount of energy given off or released per mole at the time of overlapping of atomic orbitals to form a bond. Since overlapping stabilizes the b orbital, it implies that it is a function of the distance of separation between the combining atoms. There are three major types of interaction that can be encounter when atoms come close to each other. These include,

i.   Repulsion between nuclei
ii.   Repulsion between electrons
iii.   Attraction between electron and nuclei.

The strength of overlap increases as the atoms approaches each other more closely. However, there exist a distance of closest approach such that forces of repulsion and attraction are in equilibrium. This distance is called bond length. The closer the atoms are to each other, the greater the overlap and hence the better is the strength of the bond. Consequently, molecules with shorter bond length are stronger than those with longer bond length.

The formation of hydrogen molecule can be explained using the valence bond theory. In this case, electron from the 1s orbitals of the two

hydrogen atoms overlap and form a relatively larger electron cloud called molecular orbital as shown below
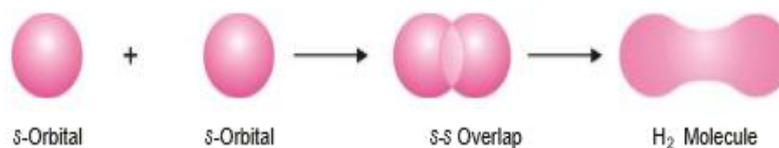
The newly form molecular orbital has energy lower than either of the two hydrogen atoms, it was formed from. Further explanation of the dependent of the strength of covalent bond in hydrogen on distance of separation can be viewed in the potential energy surface shown in Fig. 2.1.
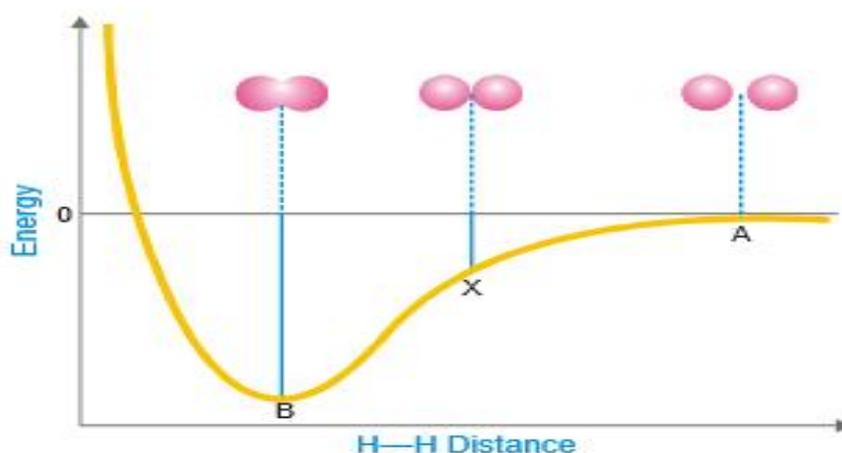

**Fig. 2.1: Potential energy diagram of hydrogen molecule**

In the diagram, at position A, the two hydrogen atoms are far from each other but as the atoms comes much closer, the energy drops until it gets to the minimum at B. After B, further decrease in distance destabilizes the molecule and leads to increase in repulsion (i.e. the energy increases). The minimum distance corresponds to the equilibrium bond length. It is at this point that maximum overlap occurs. The energy corresponding to the minimum of the curve is called dissociation energy. It is the maximum energy that stabilizes the molecule. Beyond the dissociation energy, the molecule will be destabilised.

Overlap in covalent bonded compounds can be due to sigma or pi bond depending on the molecular orbital and the orientation of the molecule before overlapping. Sigma bond can be from through one of the following overlaps

i.   s-s overlapping results from the combination of s orbital with one another. Example is the formation of hydrogen molecule

ii.   s-p overlapping occurs when an s-orbital from one atom overlap with a half-filled p-orbital from another atom. An example of molecule with s-p overlapping is in the formation of HCl and HF
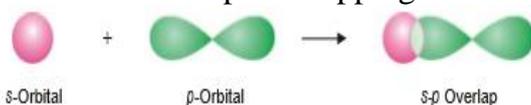
iii.   p-p overlapping can lead to sigma bond when one p-orbital from one atom overlaps with p-orbital from another orbital at the internuclear axis. Example is in the formation Cl_2, F_2, etc. (see diagram below)
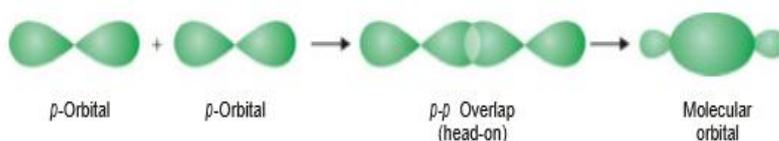
On the other hand, pi bond results from half-filled p-orbitals. The overlap occurs through lateral or sideward interaction (see diagram below). S orbital cannot form pi-bond no matter the manner they combine
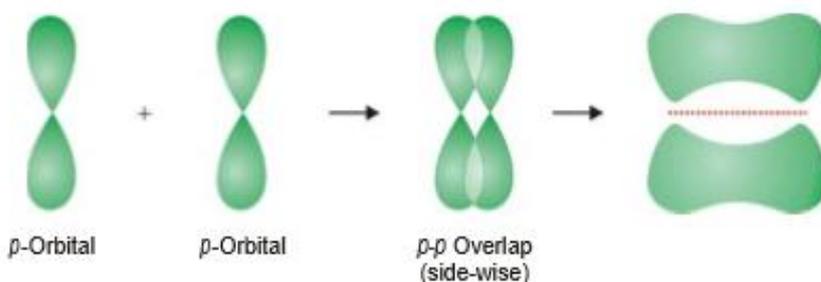
Generally, a sigma bond is stronger than a pi bond because the extent of overlap is greater during the formation of a sigma bond compared to the formation of a pi bond.

Worked example 1

(a)   Why is a sigma bond stronger than a pi bond?

(b)   State two conditions that are required before two orbitals can overlap

(c)   What is the different combination of orbitals that can lead to the formation of overlap in   sigma and pi bond. Give at least one example for each.

Solution

(a)   A sigma bond is stronger than a pi bond because the extent of overlap is greater during the formation of a sigma bond compared to the formation of a pi bond.

(b)

(i)   There must be half filled orbital from one atom to combine with half-filled orbital from the other atom to form a new orbital, having opposite spin of electron

(ii)   The atoms with bonding orbitals should be closely and properly align with the axis of their orbital

(c)   The various types of orbital overlaps for the formation of a sigma bond are,

    i.   s-s overlapping results from the combination of s orbital with one another. Example is the formation of hydrogen molecule

    ii.   s-p overlapping occurs when an s-orbital from one atom overlap with a half-filled p-orbital from another atom. E.g. is in the formation of HCl and HF

    iii.   p-p overlapping can lead to sigma bond when one p-orbital from one atom overlaps with p-orbital from another orbital at the internuclear axis. Example is in the formation Cl_2, F_2, etc

Pi overlap is formed by lateral or sideward interaction of partially filled p-orbital of one atom with p-orbital of another atom.

3.2   Hybridization theory

The valence bond theory (VBT) and the molecular orbital theory (MOT) cannot explain the formation of bonds in some atom or molecules such as carbon, helium etc. However, the concept of hybridization has been found to offer useful explanation for most cases that cannot be better explained by the VBT and MOT models. Hybridization combines atomic orbitals having comparable energies to form hybrid orbitals equal in number to the atomic orbitals from which they were formed. Some conditions required for hybridization to be feasible include the following,

(i)   Only orbital of one single atom will undergoes hybridization.

(ii)   The energy levels of the orbitals to be mixed must, be comparable

(iii)   Number of hybrid orbitals generated is equal to the number of hybridizing orbitals.

(iv)   The hybrid orbitals assume the direction of the dominating orbitals. For example, in sp   hybridization,   the   s-orbital

does not contribute towards the direction but it is the p orbitals that determine the directional character of the hybrid orbitals.
(v)   Hybridization involves the orbitals and not the electrons.
(vi) The electron waves in hybrid orbitals repel each other and thus tend to be farthest apart.

3.2.1   Types of hybridization

3.2.1.1   Sp hybridization:

Sp hybridization involves the mixing of s and p orbitals to produce two hybrid orbitals in which the s-character and p-character are equal (i.e. 50 % each). This type of hybridization is sometimes called linear hybridization and the angle of separation is 180°. Diagrammatic representation of sp hybridization is shown below
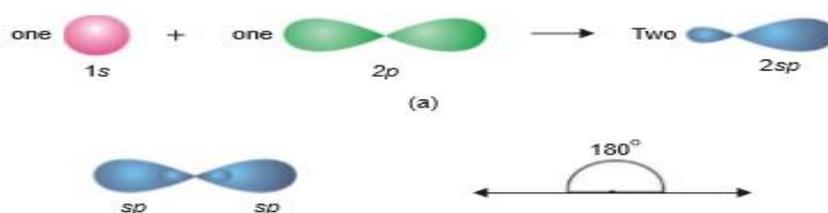

 sp orbital has two lobes (a character of p orbital) one of which is farther than the corresponding s or p orbitals and also protrudes farther along the axis. It is this bigger lobe that involves itself in the process of an overlap with orbitals of other atoms to form bonds.

Worked example 2

Explain the theory of sp hybridization in BeF_2

Solution

Example of sp hybrid orbitals is in the formation of BeF_2. The ground state electronic configuration of Be is $1s^2 2s^2 2p^{0.}$. However, when the atom is excited, one electron in the 2s valence orbital is promoted to the 2p orbital. The S and P orbital then mix and produced sp hybridized orbital which is capable of overlapping with p-orbital in fluorine to form BeF_2. As shown in the diagram below, the Be atom is at right angle to the fluorine atoms. Consequently, compounds that witness sp hybridization are linear compounds.

■ Figure 6.10
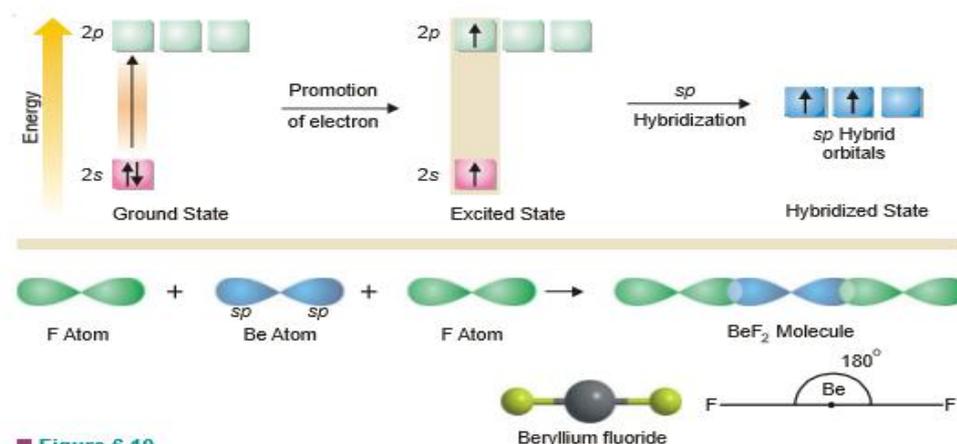
3.2.1.2   SP² hybridization

Sp² hybridization involves the mixing of one s-orbital with two p-orbitals resulting in the formation of three orbitals with 33 and 67 % s and p characters respectively. The hybrid orbitals lie on a plane father away from each other and at an angle of 120 ° as shown below. Example of compound formation that involves sp³ hybridization is BeF₃. The ground state electronic configuration of Be is $1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$. From the electronic configuration, Be is expected to form only one bond since there is only one bonding electron but the existent of compound such as BF_3, BH_3, BCl_3 contradict this principle. However, the formation of such bond is achieved through hybridization.
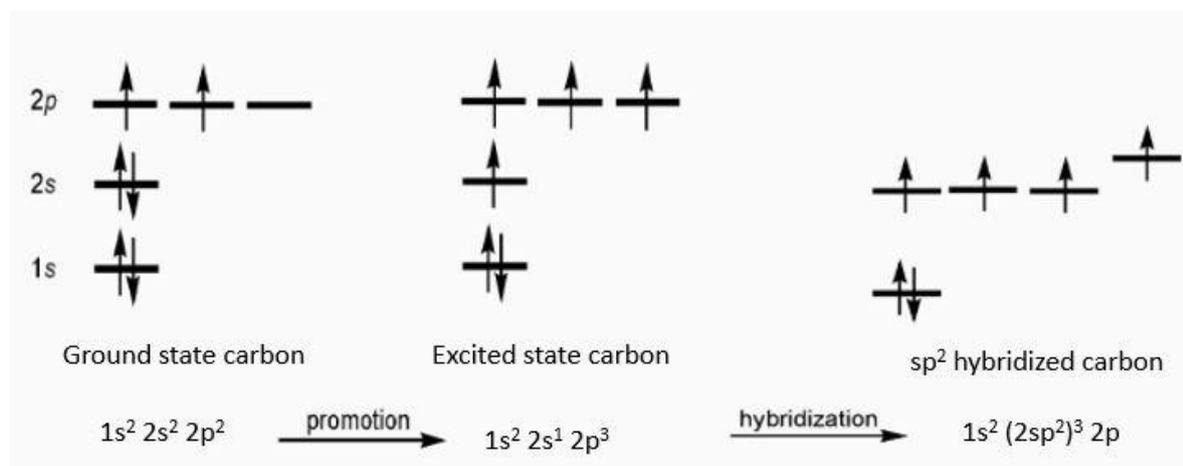
Scheme for sp² hybridization

When Be is excited, the one of the 2s electron is promoted to the 2P$_y$ level and the configuration becomes $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$. One s-orbital will then mix with 2p orbitals (P$_x$ and p$_y$) to form three hybrid orbitals by a process called sp² hybridization. The three sp² hybrid orbitals lies in one plane and subtends an angle of 120°. The three newly formed hybrid

orbitals will overlap with three p-orbitals (each supply by one atom of fluorine) to form BeF_3. The shape of sp^2 molecules is trigonal explaining why sp^2 why sp^2 hybridization is sometime called trigonal hybridization.

Boron trifluoride
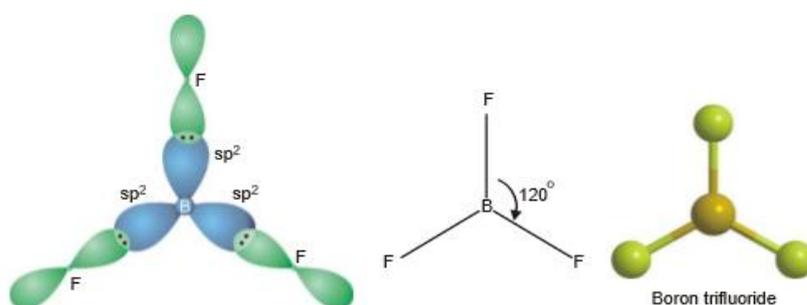
3.2.1.3   Sp³ hybridization

Sp³ hybridization has 25 % s0character and 75% p-character. It consists of four hybrid orbitals formed from one s and three p orbitals. The mixing of the four orbitals takes place in space, hence, the four hybrid orbitals would also lie in space. An arrangement in space that keeps them farthest apart is that of a tetrahedron. Consequently, each of the four hybrid orbitals are directed towards the four corners of a regular tetrahedron, sp³ hybridization is also called Tetrahedral hybridization. They are of the same shape as that of the previous two types but bigger in size. Example of molecule that can accommodate sp³ hybridization is methane (CH_4).

**Worked example 3**

Explain how carbon combine to form CH_4 in spite of the fact that its electronic configuration suggests that only two bonds can be formed.

Solution

he ground state electronic configuration of carbon is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$. The configuration suggest that carbon can only form compounds with maximum of two bonds since the configuration reveal the presence of only two bonding electrons. However, ability of carbon to form compounds that reveals it tetravalent nature contradict this principle. The formation of methane involves the promotion of one electron from 2s orbital into the p_z orbital leaving four unpaired electrons in s, p_x, p_y and p_z orbitals. These orbitals will mix and form four hybrid orbitals called sp³ hybrid orbitals and the process is called sp³ hybridization. The four hybrid orbitals will then overlap with four hydrogen atoms to form CH_4 (see scheme below). Other examples of sp³ hybridized orbitals are found in water and ammonia. In the ammonia molecule (NH_3), 2s and 2p orbitals create four sp³hybrid orbitals, one of which is occupied by a lone pair of electrons. In a water molecule, two

sp³ hybrid orbitals are occupied by the two lone pairs on the oxygen atom, while the other two bonds with hydrogen.
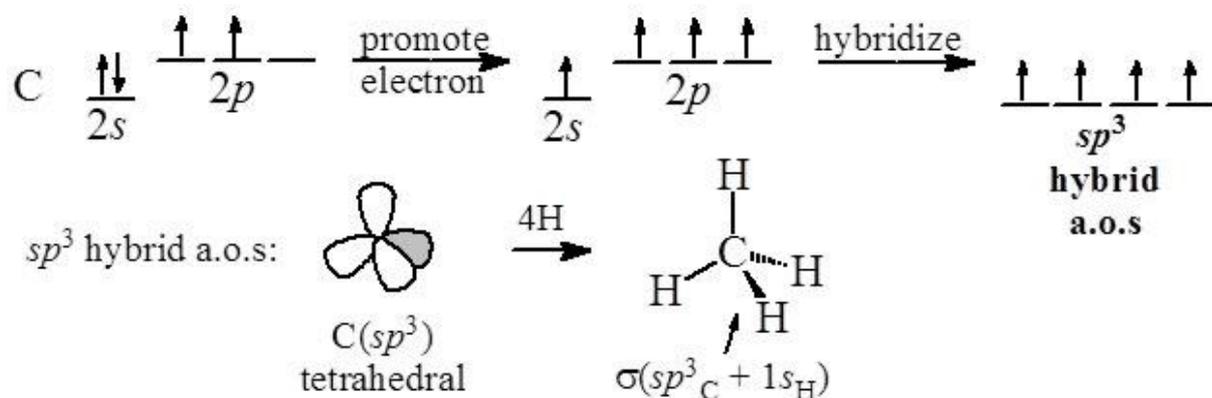
Scheme for sp³ hybridization in methane

Sp, sp² and sp³ hybridization is the basic types of hybridization. However, other types of hybridization involving d-orbitals are sp²d, sp³d, sp³d², etc. Fig. 2.2 shows how these hybridizations occur.

Worked example 4

What is the limitation of the valence bond theory?

Solution

The limitations are

(1)   The presence of other nuclei should affect the electronic arrangement of all the atoms in the molecule. The valence bod theory does not take this into account but concentrates only on the valence electron

(2)   Sometimes a single electronic structure does not explain all known properties of that molecule or ion and we have the many electronic structures called resonating structures.

(3)   Valence Bond theory fails to explain the bonding in electron deficient compounds.

(4)   It fails to explain the paramagnetic character of compounds such as oxygen molecule.
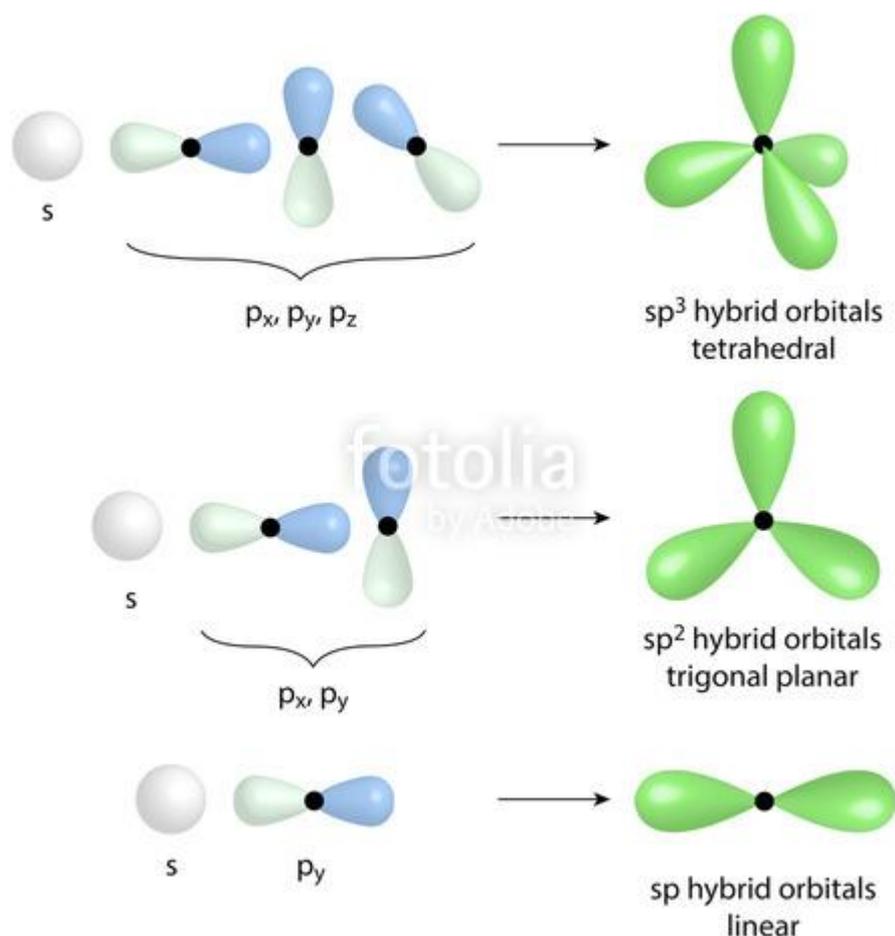
Fig. 2.2: Summary of orbitals and orbital arrangement in the three basic types of hybridization

3.3 Theory of resonance

Theory of resonance in chemistry is a theory by which the actual normal state of a molecule is represented not by a single valence-bond structure but by a combination of several alternative distinct structures. The molecule is then said to resonate among the several valence-bond structures or to have a structure that is a resonance of these structures. The energy calculated for a resonance hybrid is lower than the energies of any of the alternative structures; the molecule is then said to be stabilized by resonance. The difference between the energies of any one of the alternative structures and the energy of the resonance hybrid is designated resonance energy

The theory of resonance is based on the fundamental principle of quantum mechanics, which states that the wave function representing a stationary state of a system can be expressed as a weighted sum of the wave functions that correspond to several hypothetical structures for the system and that the proper combination is that sum which leads to a minimum calculated energy for the system.

There is sometimes an ambiguity in the location of double bonds. This ambiguity is illustrated by the Lewis structure for ozone (O_3). The following are two possible structures:

:Ö—Ö=Ö   Ö=Ö—Ö:

In such cases, the actual Lewis structure is regarded as a blend of these contributions and is written:

:Ö—Ö=Ö   ←——→   Ö=Ö—Ö:

The blending together of these structures is actually a quantum mechanical phenomenon called resonance, which will be considered in more detail below. At this stage, resonance can be regarded as a blending process that spreads double-bond character evenly over the atoms that participate in it. In ozone, for instance, each oxygen-oxygen bond is rendered equivalent by resonance, and each one has a mixture of single-bond and double-bond character (as indicated by its length and strength).

3.4   Walsh's rule

Walsh's rule was developed by Prof. A. D. Walsh while attempting to explain the explain Mulliken theory on the shapes polyatomic molecules can adopt in ground and excited states. He found that the shape polyatomic molecule adopts in their ground state depends on the number of valence electron.
The formation of molecule maybe seen as a compromise between the donation and acceptance of electron. This implies that molecular energy for the donation and acceptance of electron may vary slightly. The frontier molecular orbital theory identifies two molecular orbital energies, namely the energy of the highest occupied molecular orbital (HOMO) and that of the lowest unoccupied molecular orbital (LUMO). The theory further states that the formation of molecules involves interaction between the HOMO and the LUMO.
Walsh rule is a rule for predicting the shape of a molecule and states that a molecule will adopt a structure that best provide the most stability of its HOMO. This implies that if a structural change does not perturb the HOMO, the closest occupied molecular orbital governs the orientation of that geometry.
 Walsh diagram (also called angular coordinate diagram or correlation diagram) can be drawn through single point calculations using computational software such as Hyperchem, Gaussian, ORCA, etc. The first step is to carry out geometry optimization (i.e finding the most

stable state of the molecule-ground state). Single point calculations [(i.e., calculation of potential energy surface (PES). PES describe the energy of a system as a function of one or more parameter (such as bond length)]. Further calculations are repeated for various geometries developed from the optimized geometry through alteration of bond angle (while bond length is fixed). The Walsh diagram is plotted as a plot of molecular binding energy versus bond angle. Fig. 2.3 shows the Walsh diagram for HAH molecule.
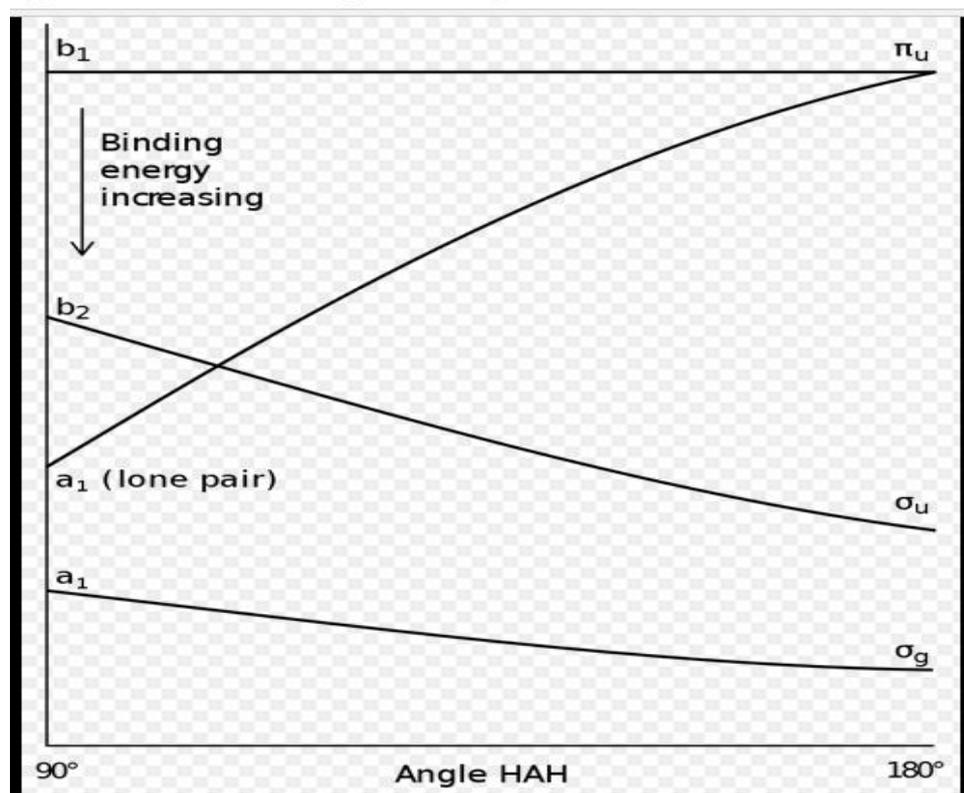
Fig. 2.3: Walsh diagram for HAH
(Source: https://en.wikipedia.org › wiki › Walsh diagram)

Worked example 5

What are the application and limitation of Walsh diagram?

Solution

Walsh diagram has some applications as follow,

(i)   Walsh diagram can explain why molecules are more stable in certain spatial configuration. For example, it can explain why water molecule prefer bent configuration. For molecules having similar valency,

(ii)   Walsh diagram can be used to explain observed regularity. The diagram also provide explanation for observe changes in geometric of a molecule with changes in valency or spin state.
(iii)   In conjunction with the molecular orbital theory, Walsh diagram can be used to predict the reactivity of a molecule

One of the major setbacks of Walsh diagram is that only the valence orbitals are considered because the core orbital usually has low energy. However, some of the valence orbital are not considered, hence the model may fail in some cases.

Other correlation diagrams commonly used are Tanabe-Sugano and Orgel correlation diagram but Walsh seems to be the most popular correlation diagram.

3.5   Molecular orbital theory (MOT)

The MOT was proposed by Hund and Mulliken in 1932 and explain the formation of molecular orbital through the combination of individual atomic orbitals with each other. The theory explains that the formation of molecule considers that the combining electrons in the atomic orbitals do not belong to a particular bond but spread throughout the entire molecule. According to the MOT, a molecular orbital is a system constructed from linear combination of atomic orbitals. This combination give rise to two main types of orbitals (i.e. the bonding and anti-bonding molecular orbitals). The bonding molecular orbital arises from the constructive overlaps of neighbouring atomic orbitals while anti bonding molecular orbital arises from the destructive overlap of neighbouring atomic orbitals.

3.5.1 Linear combination of atomic orbital (LCAO)

Linear combination of atomic orbital provides a theoretical approach of using the wave function to represent the formation of molecular orbital through appropriate atomic orbitals. If a wave function for a 1S electron belonging to an atom, A is $\psi_{(1S)}(A)$ and $\psi_{(1S)}(B)$ describes the wave function for a 1s electron found in atom B. The overall wave function for the system must be written as a superposition of the two atomic orbitals (equation 2.1),

$$\psi = N[\psi_{(1S)}(A) + \psi_{(1S)}(B) \qquad 2.1$$

where N is the normalization factor. The wave function resulting from superposition of different atomic wave function (as expressed in equation 2.1) is called linear combination of atomic orbital (LCAO). An approximate molecular orbital formed from a LCAO is called linear

combination of atomic orbital-molecular orbital (LCAO-MO). According to the Schrodinger model, the square if the wave function (i.e., $|Œ|^2$) represents the probability density. Therefore, the probability density of the LCAO-MO of a 1s σ-orbital can be written as,

$$|Œ|^2 = N^2 \left[\psi_{(1S)}(A) + \psi_{(1S)}(B) \right]^2 \qquad 2.2$$

$$= N^2 \left[\psi_{(1S)}(A)^2 + \psi_{(1S)}(B)^2 + 2\psi_{(1S)}(A)\psi_{(1S)}(B) \right]$$
2.3

Equation 2.10 has three components which can be explained as follows.

i. $Œ_{(1S)}(A)^2$, which represent the probability density of electron confined to the orbital, A.

ii. $Œ_{(1S)}(B)^2$, which represents the probability density of electron confined to the orbital, B.

iii. $2Œ_{(1S)}(A)\psi_{(1S)}(B)$, which is the extra contribution to the density of electron and is called overlap density.

The overlap density also represents an enhancement of the probability of finding electrons in the internuclear region above what it would be if they were confined to one of the two atoms. This enhancement is also called constructive interference of the two atomic orbitals. Similar analogy can be extended to antibonding molecular orbital. The expression representing the formation of antibonding molecular orbital arising from combination of atomic orbitals of atoms A and B can be written as,

$$Œ' = N[Œ_{(1S)}(A) - \psi_{(1S)}(B) \qquad 2.4$$

LCAO-MO for the above wave function correspond to a molecular orbital having energy higher than any of the contributing orbitals. Therefore, antibonding molecular orbital increases the energy of a system Whereas bonding molecular orbital is associated with constructive interferences, antibonding molecular orbital is associated with destructive interference. The probability function of antibonding molecular orbital can also be derived as it was done for bonding molecular orbital, hence we have

$$|Œ'|^2 = N^2 \left[\psi_{(1S)}(A) - \psi_{(1S)}(B) \right]^2 \qquad 2.5$$

$$= N^2 \left[\psi_{(1S)}(A)^2 + \psi_{(1S)}(B)^2 - 2\psi_{(1S)}(A)\psi_{(1S)}(B) \right]$$
2.6

It can be seen that the first two terms in equation 2.6 are the same as in those obtained for bonding molecular orbital and their significant is the same. However, the difference is in the sign of the third term, which is positive for bonding molecular orbital and negative for antibonding

molecular orbital. The negative value (i.e. $[-2 E_{(1S)}(A)\psi_{(1S)}(B)]$ clearly signify the factor that contribute to reduce the probability of finding electron between the nuclei. Antibonding orbital raises the energy of the molecule relative to the separated atom and destabilizes the molecule relative to the separated atoms whereas bonding electron stabilizes the molecule.

A combination of N number of atomic orbitals will yield N number of molecular orbitals. There are two types of molecular orbitals, including binding and antibonding molecular orbitals. Several combinations of s or p electron can form bonding or antibonding molecular orbital. The formation of these molecular orbitals involves combination of valence electrons in the respective atomic orbitals. For example, combination of two hydrogen atoms to form hydrogen molecules involves two 1s-electrons combining with each other as shown below.
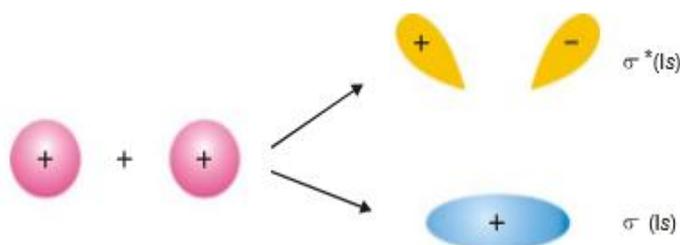

The wave functions either have (+) or (–) sign. The positive sign shown on 1s orbitals of hydrogen atoms reveals that these orbitals are spherically symmetrical and their wave functions are associated with +ve sign in all directions. In case of p-orbitals one lobe has +ve sign while other has –ve sign. The overlapping of atomic orbitals takes place if they have similar signs on their lobes

The combination generates two set of molecular orbitals. The first is called sigma bonding molecular orbital i.e. σ(1s) and sigma antibonding molecular orbital, σ*(1s). As can be seen in the above diagram, σ*(1s) molecular orbital is positioned at a higher energy level than the σ(1s) molecular orbital. This confirms that the bonding molecular orbital contributes to the lowering of the energy of a molecule and hence stabilizes the system while the antibonding molecular orbital increases the energy of the system and thus tend to destabilize the system. A sigma (σ) electron is an electron that occupies a sigma orbital. Sigma orbitals can also be formed from combination of p_Z orbitals (z is assumed to be the internuclear axis) as shown in the diagram below,
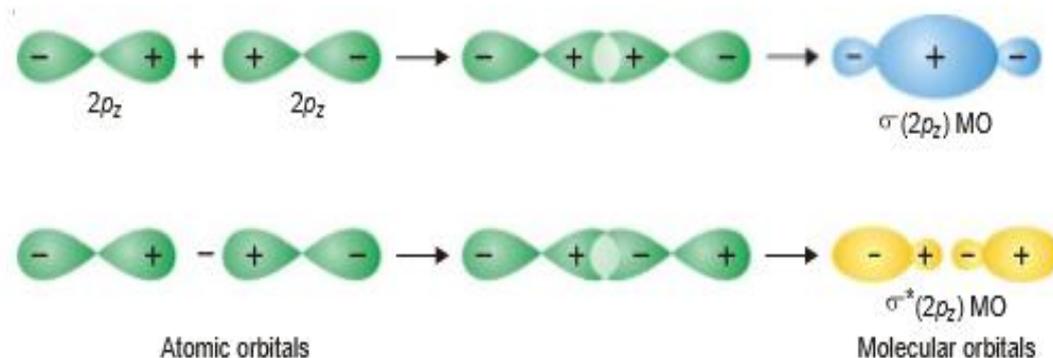
Apart from sigma orbitals, P_Y and P_x orbitals can combine to give pi-bonding and pi antibonding molecular orbitals as shown below,
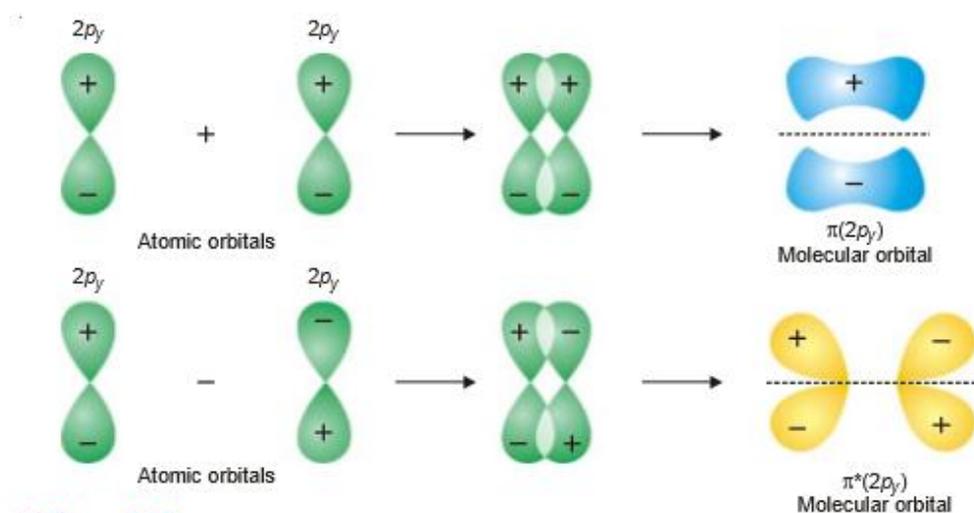
From the above, (2p$_y$) is pi bonding molecular orbital and is formed when similar charges on the 2p$_y$ orbitals meet side by side while *(2p$_y$) (that is the pi anti bonding molecular orbital) is formed when the adjacent charges are not similar. Since P$_x$ and P$_y$ sub orbitals are degenerate orbitals because they have similar energy, bot bonding or antibonding molecular orbitals arising from them will also be degenerate. The (2p$_y$) and (2p$_x$) bonding molecular orbitals have zero electron density on the plane that contain the nuclear axis but the electron density is concentrated above and below the nodal region. The * (2P$_y$) and * (2P$_x$) antibonding molecular orbitals have higher energy than their corresponding molecular and atomic orbitals.

It can be stated that different molecular orbitals have different energy level. For example, the energy of bonding molecular orbital varies in the following order, σ(1s) σ(2s) σ(2p$_Z$) (P$_y$) (P$_x$) while the order for the antibonding molecular orbital is σ*(1s)σ*(2s) σ*(2p$_Z$) (*P$_y$) *(P$_x$). However, (*P$_y$) and *(P$_x$) are degenerate orbitals just like (P$_y$) and

(P$_x$) orbitals. The diagram below presents a pictorial trend for the variation of energy of the bonding and nonbonding molecular orbitals.
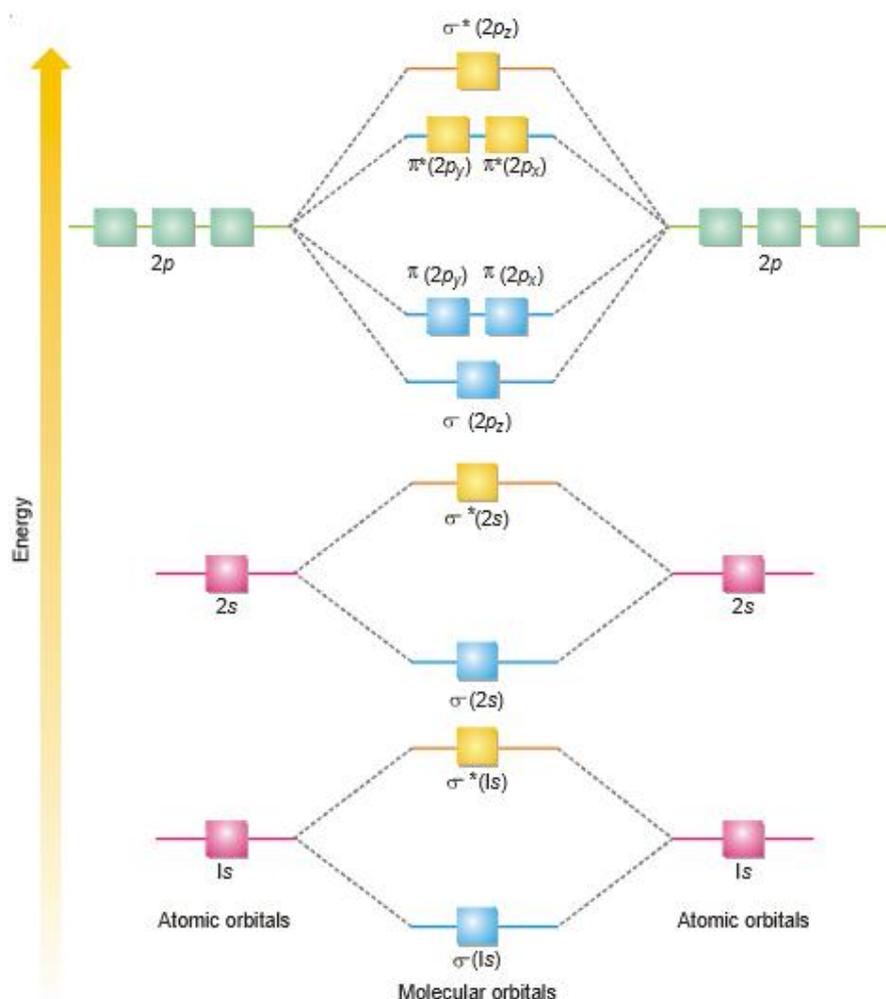
s and P$_Z$ orbital can combine end to end to form sigma bonding and sigma antibonding molecular orbitals as shown below
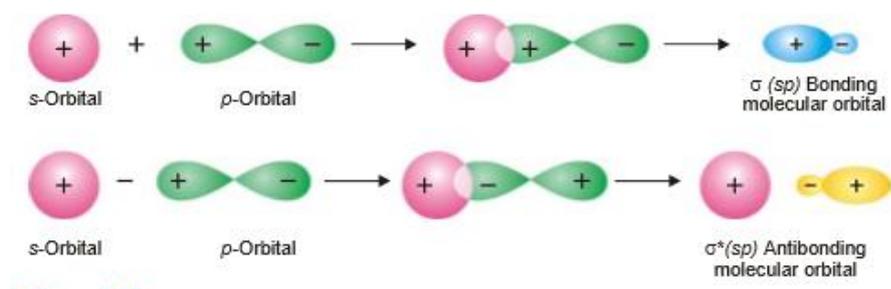
However, s-orbital cannot form a sigma molecular orbital with P$_y$ or P$_x$ because they do not have the same symmetry about the internuclear axis.

Generally, the following conditions must be fulfilled before molecular orbitals can be formed,

(i)   The energies of the combining atomic orbitals should be comparable. For homonuclear diatomic molecules similar atomic orbitals combine to form molecular orbitals. For example, 1s from one atom can combine with 1s atomic orbital from another atom to form molecular orbital. However, Is cannot combine with 2s because the energy is not comparable

(ii)   Overlap between atomic orbitals should be considerable significant. The greater the overlap between the atomic orbitals, greater is charge density between the nuclei.

(iii)   The symmetry of the combining atomic orbitals should be the same. The atomic orbitals should have the same symmetry about the internuclear axis. For example, 2s orbital of one atom can combine with 2s or $2P_z$ orbital of another atom but not with the $2P_y$ or $2P_x$ orbital. Molecular orbitals that can be formed from combination of possible atomic orbitals are presented in the Table 2.1 below,

Table 2.1: Combination of atomic orbitals and their corresponding molecular orbitals

Atomic orbital 1	Atomic orbital 2	Molecular orbital
s-orbital	s-orbital	σ (sigma) orbital
s-orbital	P_Z orbital	σ (sigma) orbital
P_Z orbital	P_Z orbital	σ (sigma) orbital
P_x orbital	P_x orbital	(pi) orbital
P_y orbital	P_y orbital	(pi) orbital

The formation of bonding molecular orbital can be viewed as addition of electron waves (i.e. constructive interference) while the formation of antibonding molecular orbital is a product of subtraction of electron wave. Fig. 2.4 shows the variation of molecular energy with internuclear distance for both bonding and antibonding molecular orbital. The distance corresponding to the minimum of the curve for bonding molecular orbital is the equilibrium bond length (r_e) and the corresponding energy is the dissociation energy (D_e). For example, the theoretical values of r_e and D_e for hydrogen molecular ion are 130 pm and 1.77 eV respectively.
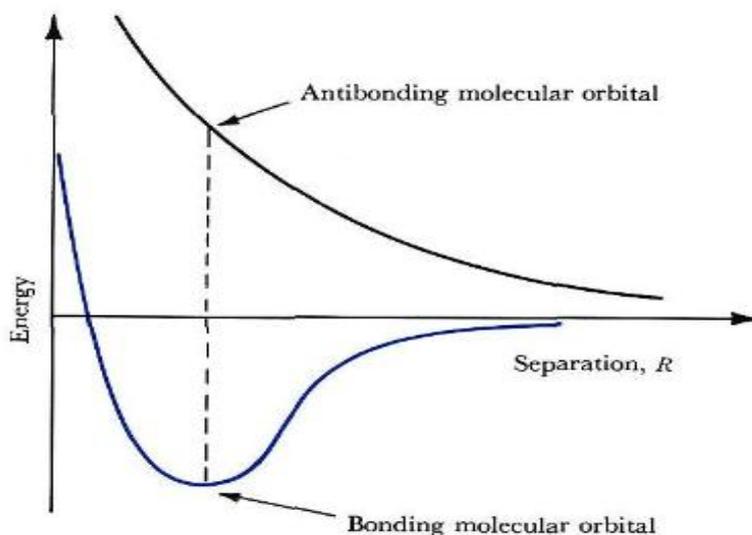
Fig. 2.4: Variation of energy with R for bonding and antibonding molecular orbital

Repulsive forces dominate during the formation of an antibonding molecular orbital. However, during the formation of a bonding molecular orbital the energy starts decreasing and reaches to a minimum value which corresponds to the bond length between the two atoms (r_0). At a distance less than r_0 the repulsive forces start dominating over the attractive forces and energy starts increasing

The term bond order (b) is often use to predict the stability of a molecule. Bond order, b is defined as half the difference between the number of electrons in the bonding molecular orbital (n) and the electrons antibonding molecular orbital (n*). That is b = ½ (n = n*). The greater the bond order, the more stable is the compound. Generally, bond order greater than unity points toward stability whereas bond order less than unity points toward instability.

Apart from the s-electrons described above, p-electrons also contribute to the formation of molecular orbital. P-orbital has three degenerate orbital (P_x, P_y and P_z) which are perpendicular to each other and can overlap constructively or destructively giving rise to pi ( ) bonding and anti-pi (*) bonding molecular orbitals respectively.

44

Worked example 6

In a Tabular form, state five differences between bonding and antibonding molecular orbitals

Bonding molecular orbital	Antibonding molecular orbital
The wig m function is $\mathcal{E}' = \frac{1}{N\Gamma}\mathcal{E}_{(1s)(\angle A) -}$ ... $\mathcal{E}_{(1s)(B)}$ m from const	The windir function is $\mathcal{E}' = \frac{1}{N\Gamma}\mathcal{E}_{(1s)(\angle A) -}$ $\mathcal{E}_{(1s)(B)}$ med from
Form from constructive (or addition) overlap of atomic orbitals	Formed from destructive(subtraction) overlap of atomic orbitals
Formed when the lobes of atomic orbitals have same signs	Formed when the lobes of atomic orbitals have different signs
Energy is lower than that of the combining atomic orbitals	Energy is higher than that of the combining atomic orbitals
The electron density is high in the region between the nuclei of bonded atoms	Electron density is low in the region between the nuclei and bonded atoms
Every electron in bonding MO contributes towards the attractive force	Electrons in antibonding molecular orbital contributes to repulsive force
Stabilizes the molecule	Destabilizes the molecule

Solution

The strength of a chemical bond depends to some extent, on the nature of orbital overlap. Strong bonds results from combination of orbitals that have similar or nearly similar energies. In homonuclear diatomic molecule, the energy of the 2S orbital of the two atoms are the same and so is the energy of the 2P orbitals of the two atoms. Therefore, the 2S orbital will formed a strong overlap and so will the 2P orbital also yield strong overlap because the respectively orbitals, which have similar energies. These overlaps will contribute to a sigma orbital. It is the convention of quantum mechanics to write a sigma orbital in terms of all the orbitals that have symmetry to contribute to the final orbital. This is represented in equation 2.7

$$\psi = C_{2S}(A)\psi_{2S}(A) + C_{2P}(A)\psi_{2P}(A) + C_{2S}(B)\psi_{2S}(B) + C_{2P}(B)\psi_{2P}(B) \qquad 2.7$$

where Cs are the various orbital coefficient.

Worked example 7

(a)   In a Tabular form, state four differences between sigma and Pi molecular orbitals
(b)   What is common between pi and sigma molecular orbitals

Solution

(a)

Sigma molecular orbital	Pi molecular orbital
Formed by head to head overlapping of atomic orbitals.	Formed by sideward overlapping of P_x or P_y atomic orbitals
The overlap is along internuclear axis.	Overlap is perpendicular to internuclear axis
This orbital is symmetrical to rotation about the line joining the two nuclei.	Orbital is not symmetrical to rotation about the line joining the two nuclei.
The region of overlap is greater leading to the formation of strong bond	Region of overlap is less resulting in the formation of weak bond.

(b)   The common feature is that they are both formed from proper combination of atomic orbitals, leading to the formation of overlap.

3.6   Bond order

The term bond order (b) is often use to predict the stability of a molecule. Bond order, b is defined as half the difference between the number of electrons in the bonding molecular orbital (n) and the electrons in the antibonding molecular orbital (n*). That is b = ½ (n = n*). The greater the bond order, the more stable is the compound. Generally, bond order greater than unity points toward stability whereas bond order less than unity points toward instability. Let us calculate bond order of some molecules as shown below,

Worked example 8

Apply the molecular orbital theory to explain bonding in the following molecules

(i)   Hydrogen molecule
(ii)   Helium molecule
(iii)   Oxygen molecule

In each case, calculate the bond order and comment on the result obtained from the calculation

i.   Hydrogen molecule

Hydrogen molecule has two electrons, each contributed by 1s orbital. According to the Aufbau principle, the lowest level must first be filled before the higher level. The molecular orbitals formed between the two hydrogen atomic orbitals are sigma bonding and sigma antibonding molecular orbitals,

$$H(1s^1) \;+\; H(1s^1) \;\rightarrow\; H_2\sigma\,(1s^2), \sigma^*(1s^0)$$

Consequently, the number of electrons in bonding molecular orbital is two while the number in antibonding molecular orbital is zero. Therefore, the bond order of hydrogen molecule is

$$b\,(H) = \frac{n - n^*}{2} = \frac{2 - 0}{2} = 1$$

The calculated bond order indicate that two hydrogen atoms are bonded together by only one bond to form hydrogen molecule. The formation process can be represented as shown in the diagram below,
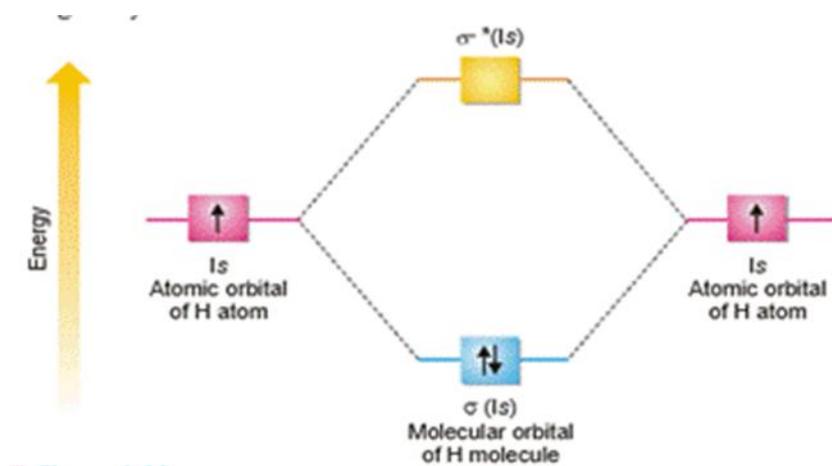
ii.   Helium

Helium has atomic number of two, hence two electrons. When two helium atoms combine, four electrons will be formed. The molecular orbital formed is developed from combination of two 1s atomic orbitals. That is a total of two molecular orbitals would be formed Thus

$$H\iota\,(1s^2) \;+\; H\iota\,(1s^2) \;\rightarrow\; H\iota_2\sigma\,(1s^2), \sigma^*(1s^2)$$
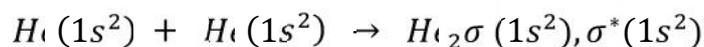
Therefore, the bond order for helium is

$$b\,(H\iota) = \frac{n - n^*}{2} = \frac{2 - 2}{2} = 0$$

Calculated bond order of zero indicate that the molecule cannot exist.
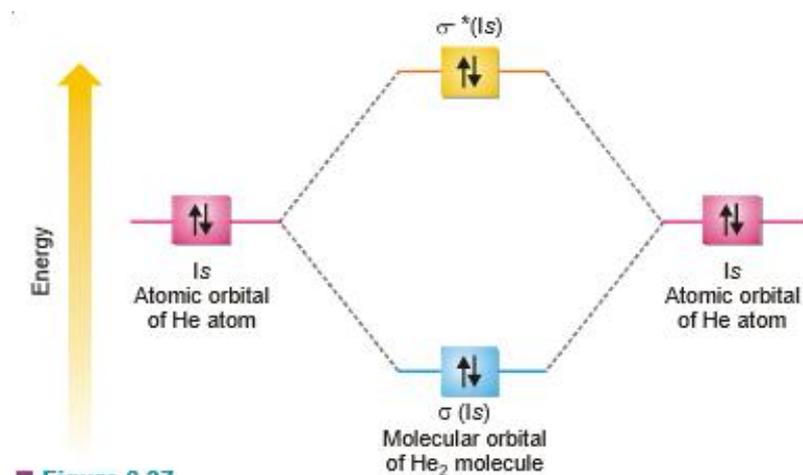
iii.   Oxygen molecule

The electronic configuration of oxygen is $1s^2 2s^2 2P_z^1 2P_y^1 2P_y^1$. In this case, only the 2s and 2p orbitals would be involved in bonding (i.e. valence shell) giving a total of five electrons for each contributing oxygen atom and 6(2) =12 for the oxygen molecule. The equation can be written as,

$$O \ (1s^2 2s^2 2P_z^2 2P_y^1 2P_y^{1)} + O \ (1s^2 2s^2 2P_z^2 2P_y^1 2P_y^1)$$
$$\rightarrow O_2 \sigma(2s^2)\sigma^*(2s^2)\sigma(2p_z^2)\pi(2p_y^2)\pi(2p_x^2)\pi^*(2p_y^1)\pi^*(2p_x^1)$$
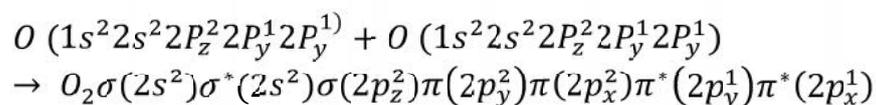
From the molecular orbital configuration is $\sigma(2s^2)\sigma^*(2s^2)\sigma(2p_z^2)\pi(2p_y^2)\pi(2p_x^2)\pi^*(2p_y^1)\pi^*(2p_x^1)$ indicating that the number of bonding electron is 8 while the number of antibonding electron is 4 (see diagram below). Therefore, the bond order is

$$b \ (O) = \frac{n - n^*}{2} = \frac{8 - 4}{2} = 0$$

The calculated bond order of 2 indicate that oxygen molecule is stable (n>n*) and from the above diagram, there are unpaired electrons hence it is paramagnetic.
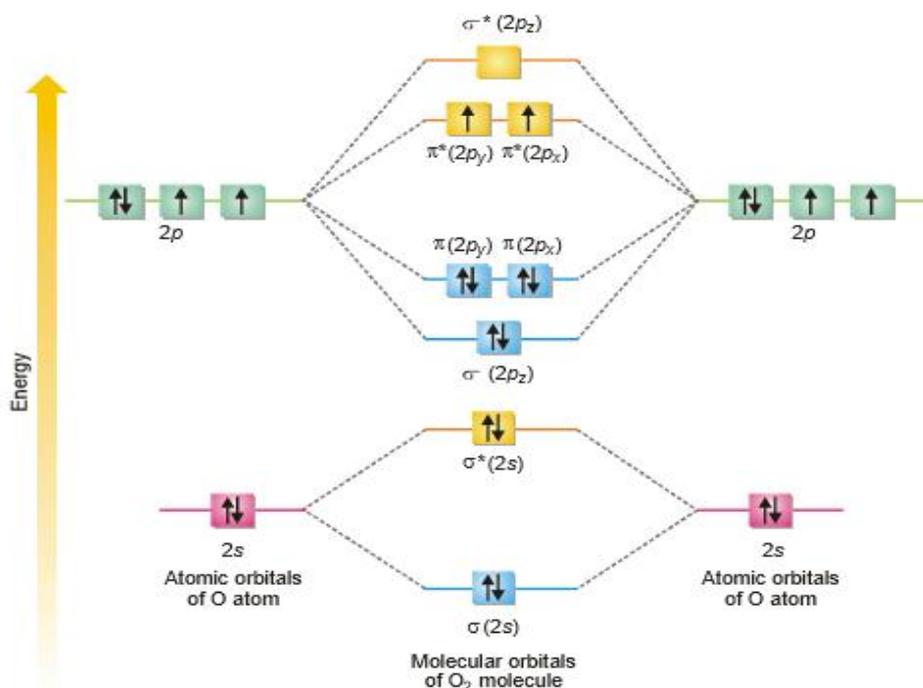
Worked example 9

(a) Calculate the bond order of nitrogen molecule from first principle. Also present a diagram to indicate how the bonding electrons are distributed. Is the molecule stable? Give reason for your answer. (b) Is N_2 paramagnetic or diamagnetic. Give reason for your answer.

Solution

(a) Nitrogen atom has seven electrons and its electronic configuration is $1s^2 2s^2 2P_z^1 2P_y^1 2P_y^1$ indicating that the valence shell configuration is $2s^2 2P_z^1 2P_y^1 2P_y^1$. This gives five electrons and a total of ten electrons (i.e. 2 x 5=10) when they combine with one another. The formation of molecular orbital occurs according to the following equation,

$N + N$

$\rightarrow N_2 \sigma(2s^2)\sigma^*(2s^2)\sigma(2p_z^2)\pi(2p_y^2)\pi(2p_x^2)\pi^*(2p_y^0)\pi^*(2p_x^0)\sigma^*(2p_z^0)$
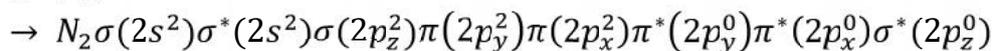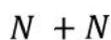
In this case the number of bonding electrons is eight (8) while the number of nonbonding electrons is four (4). Therefore, the bond order is

$$b\,(N) = \frac{n - n^*}{2} = \frac{8 - 2}{2} = 3$$

The molecule (N_2) is stable because the bond order is positive. i.e. n>n*. A diagram showing the distribution of electrons into the various bonding and antibonding orbitals is shown below
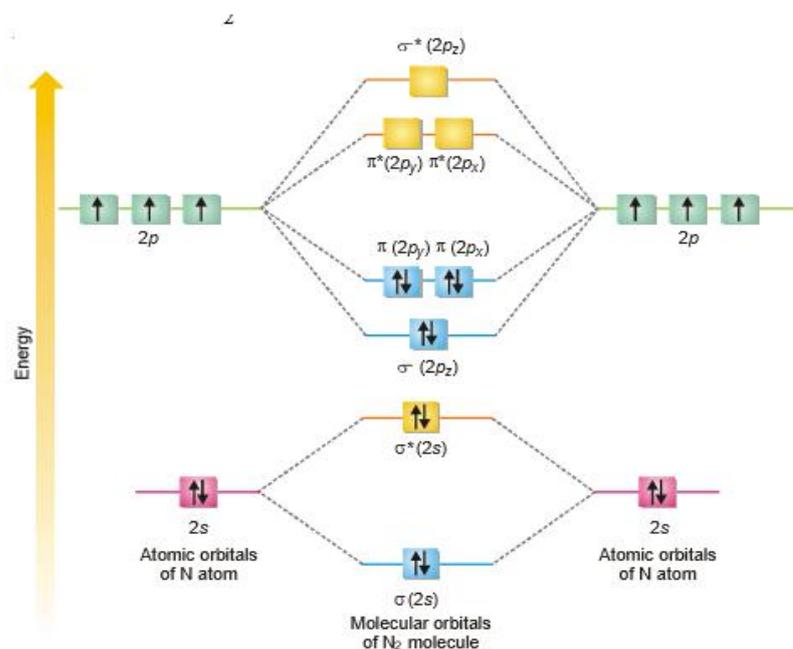
(b) From the above diagram, it can be seen that N_2 is diamagnetic because all the electrons are paired

Worked example 10

Show from first principle that beryllium cannot exist as a molecule

Solution

Beryllium is the fourth element in the periodic Table. It has four electrons indicating that its electronic configuration is $1s^2 2s^2$. This means eight electrons will be used for the formation of molecular orbital (i.e. each atom contributes 4). Consequently, the formation of molecular orbital will take place according to the following equation

$$Be + Be \rightarrow Be_2 \sigma(2s^2)\sigma^*(2s^2)\sigma(2p_z^2)\sigma^*(2p_z^2)$$
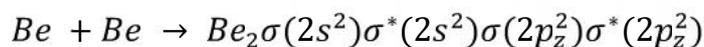
From the above, the number of bonded electrons is 4 while the number of nonbonding electrons is also equal to 4. Hence the bond order is

$$b\,(Be) = \frac{n - n^*}{2} = \frac{4 - 4}{2} = 0$$

Since the calculated bond order is xero, Be_2 does not exist

Worked example 11

What are the four major information that can be deduced from bond order of a molecule

Solution

(1)   Stability of the Molecule/Ion: A molecule/ion is stable if n > n*, i.e. when the bond order is positive. However, when the bond order is negative, the molecule is not stable and when the bond order is zero, the molecule does not exist.

 (2)   Bond Dissociation Energy The greater the bond order, the greater is the bond dissociation energy.

(3)   Bond Length Bond order is inversely proportional to bond length. Bond length increases as the bond order decreased.

(4)   Magnetic Properties The presence of unpaired electrons in molecular orbitals of a species makes it paramagnetic in nature. Greater the number of unpaired electrons, the more will be its paramagnetic character. On the other hand, if there are no unpaired electrons in the species will be diamagnetic in nature.

3.7   Bond order for heteronuclear diatomic molecule

Heteronuclear molecules are formed from combination of two dissimilar atomic orbitals. This means each atomic orbital contributes unevenly to the molecular orbital. The wave function for the molecular orbital of heteronuclear diatomic molecule can be written as

$$\Psi_{MO} = C_1 \psi_1 + C_2 \psi_2$$

In developing molecular orbitals for heteronuclear molecule, the bonding molecular orbital is made close to electronegative atom while the antibonding molecular orbital is close to the electropositive atom. A common example of hetero nuclear diatomic molecule is NO. The molecule is formed from N and O. Their electronic configuration is,

$$N = 1s^2 2s^2 2P_z^1 2P_y^1 2P_y^1$$
$$O = 1s^2 2s^2 2P_z^2 2P_y^1 2P_y^1$$
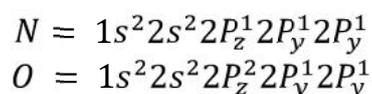
The number of valence electron in nitrogen is 5 and 6 for oxygen. This gives a total of 11 valence electrons. The configuration of molecular orbital of NO can be written as,

$$N + O \rightarrow NO\ \sigma(2s^2)\sigma^*(2s^2)\sigma(2p_z^2)\pi(2p_y^2)\pi(2p_x^2)\pi^*(2p_y^1)$$
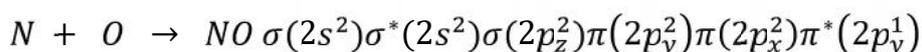
The total number of bonded electrons is 8 while the total number of nonbonding electrons is 3. Therefore, the bond order for NO is

$$b\,(NO) = \frac{n - n^*}{2} = \frac{8 - 3}{2} = 2.5$$

Molecular orbital diagram is shown below
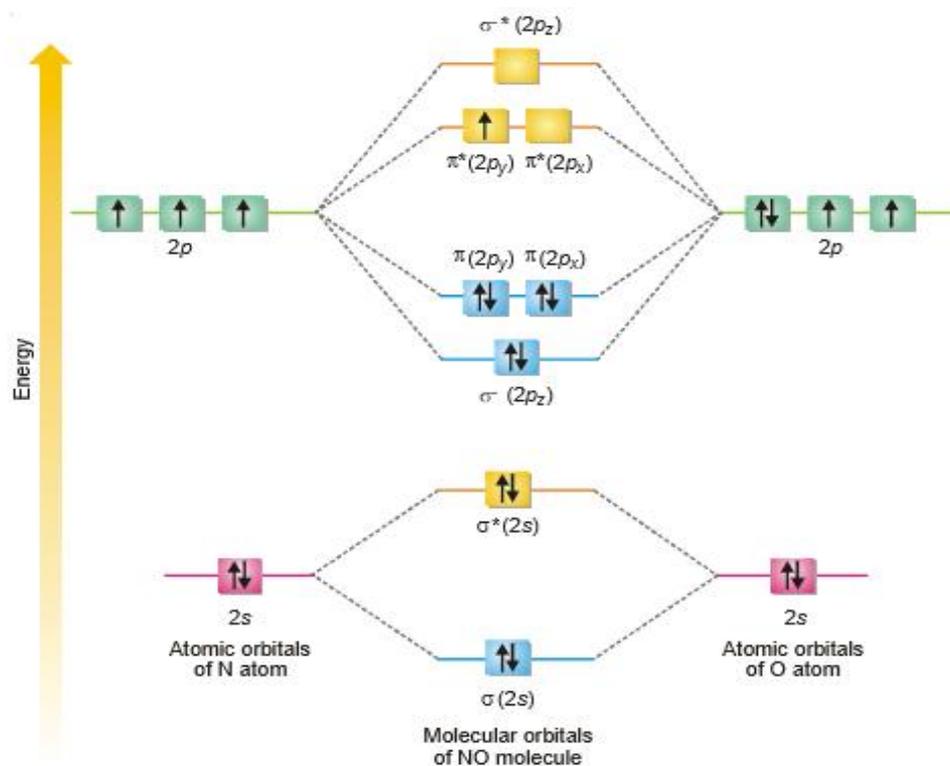
From the above, NO is stable because n>n*. No is paramagnetic because not all its electrons are paired.

3.8   Theory of bonding in some systems

3.8.1 Theory of bonding in hydrogen molecular ion

Under the MOT treatment, the hydrogen molecular ion is the simplest molecule that can be considered. In the MOT approach, the formation of molecule is pictured as situation in which the combining electron do not belong to a particular bond but spread throughout the entire molecule. Consequently, according to the MOT, a molecular orbital is a system constructed from linear combination of atomic orbitals, which results in two main types of orbitals (i.e. the bonding and anti-bonding molecular orbitals). The bonding molecular orbital arises from the constructive overlaps of neighbouring atomic orbitals while anti bonding molecular orbital arises from the destructive overlap of neighbouring atomic orbitals. This approach can be simplified by considering two nuclei, A and B separated by a distance, R as shown Fig. 2.5.
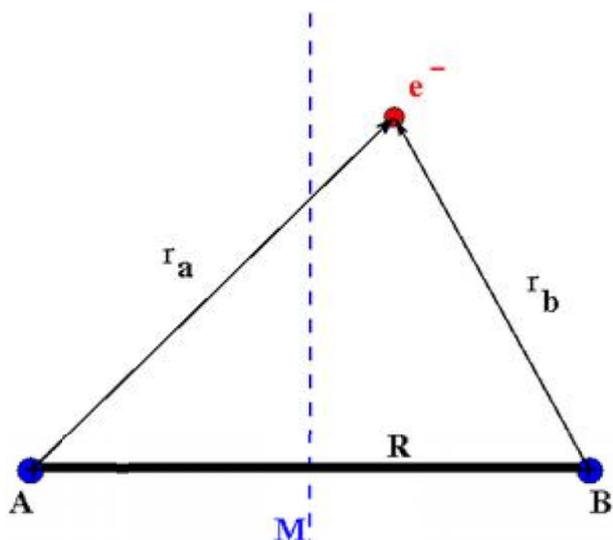
Fig. 2. 5: Diagram showing distant of nuclei (A and B) from electron in H_2^+

The Hamiltonian for this system can be written as follows,

$$\widehat{H} = \frac{-\hbar^2}{2m_e}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) + U = \frac{-\hbar^2}{2m_e}\nabla^2 + U \qquad 2.8$$

The force of attraction arising from interaction between electron and the nuclei will be inversely proportional to the distance of separation and is given by,

$$\frac{-e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b}\right)$$
$$2.9$$

On the other hand, the repulsive interaction between the nuclei is given as,

$$\frac{e^2}{4\pi\varepsilon_0} \times \frac{1}{R}$$
$$2.10$$

The potential energy of the system will be the sum of the forces of attraction and repulsion as expressed in equation 2.11

$$U = \frac{-e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right)$$
$$2.11$$

Substituting for U in equation 2.8, equations 2.12 and 2.13 are obtained,

$$\widehat{H} = \frac{-\hbar^2}{2m_e}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right)$$
$$2.12$$

$$= \frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right)$$
$$2.13$$

Equation 2.13 can further be inserted into the Schrödinger equation to obtained equation 2.14, which expresses the Schrödinger equation for hydrogen molecular ion,

$$\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right)\right]\psi = E\psi$$
$$2.14$$

The one electron wave function obtained by solving the Schrödinger equation is called molecular orbital. A molecular orbital is significant because through the function, $|Œ|^2$, it gives the probability of finding electron in the molecule.

Worked example 12

Consider two atomic nuclei (A and B) separated from each other by a distance equal to R. If the distant of A and B from electron are r_a and r_b. Answer the following questions

i.   Write an expression for the Hamiltonian of the system
ii.   What is the force of attraction and repulsion for this system?
iii.   Write an expression for the potential energy of the system
iv.   Write expression for the Schrodinger equation of this system

From your results, define the term, molecular orbital and state its significant

Solution

i.   The Hamiltonian for this system can be written as follows,

$$\hat{H} = \frac{-\hbar^2}{2m_e}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) + U = \frac{-\hbar^2}{2m_e}\nabla^2 + U \qquad 1$$

ii.   The force of attraction arising from interaction between electron and the nuclei will be inversely proportional to the distance of separation and is given by,

$$\frac{-e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b}\right)$$
$$2$$

On the other hand, the repulsive interaction between the nuclei is given as,

$$\frac{e^2}{4\pi\varepsilon_0} \times \frac{1}{R} \qquad 3$$

iii.   The potential energy of the system will be the sum of the forces of attraction and repulsion as expressed in equation 4

$$U = \frac{-e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right) \qquad 4$$

Substituting for U in equation 1, equations 5 and 6 are obtained,

$$\hat{H} = \frac{-\hbar^2}{2m_e}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right) \qquad 5$$

$$= \frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right) \qquad 6$$

iv.   Equation 6 can further be inserted into the Schrödinger equation to obtained equation 7, which expresses the Schrödinger equation for hydrogen molecular ion,

$$\left[\frac{-\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_a} + \frac{1}{r_b} + \frac{1}{R}\right)\right]\psi = E\psi$$

7

The one electron wave function obtained by solving the Schrödinger equation is called molecular orbital. A molecular orbital is significant because through the function, $|Œ|^2$, it gives the probability of finding electron in the molecule.

3.8.2 Theory of bonding in hydrogen atom

The potential energy for the hydrogen atom can be written as,

$$V = \frac{-e^2}{4\pi\varepsilon_0 r}$$

The expression does not contain the Cartesian coordinate (i.e. xyz) but r which is a spherical polar coordinate. The task of simplifying the therefore entails, conversion of the Cartesian coordinate to the polar coordinate. While the Cartesian coordinate deals with xyz, the polar coordinate in this case will also involves three parameters, namely, r, ϕ and θ. The relationship between r and the Cartesian system can be written as,

$$r^2 = x^2 + y^2 + z^2$$
$$r = \sqrt{x^2 + y^2 + z^2}$$

In spherical polar coordinates, r is the length of the radius vector from the origin to a point (xyz). In order to present analytical solution, let us consider a system involving both the polar and the Cartesian coordinate as shown in Fig. 2.6,
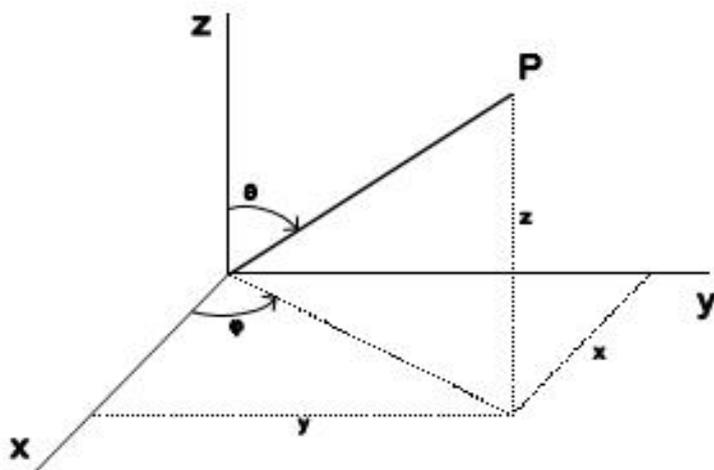
Fig. 2.6: Coordinate of hydrogen atom

The angle between the z axis and the radius is θ while the angle between projection of the radius vector onto the xy plane and the +x axis is given as φ, From the diagram,

$$cos\theta = \frac{z}{r} = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\theta = Cos^{-1}\frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$tan\varphi = \frac{y}{x}$$

$$\varphi = tan^{-1}\frac{y}{x}$$

Consequently, $x = r\sin\theta cos\varphi$, $y = r\sin\theta\sin\varphi$ and $z = rcos\theta/$
The Schrödinger equation can be written as,

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

In spherical polar coordinate the Schrödinger equation becomes,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) + \sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{s\psi}{d\theta}\right) + \frac{d^2\psi}{d\varphi^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

When the potential energy is introduced, the equation becomes,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) + \sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{s\psi}{d\theta}\right) + \frac{d^2\psi}{d\varphi^2} + \frac{2m}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)\psi = 0$$

Worked example 13

i.   Write expression for the potential energy of hydrogen atom. What is the shortcoming of the equation if it is to be used for solving the Schrodinger equation for the hydrogen atom?
ii.   How can you overcome the challenges?
iii.   Use the diagram below to derive the relationship between polar and cartesian coordinate system for hydrogen atom
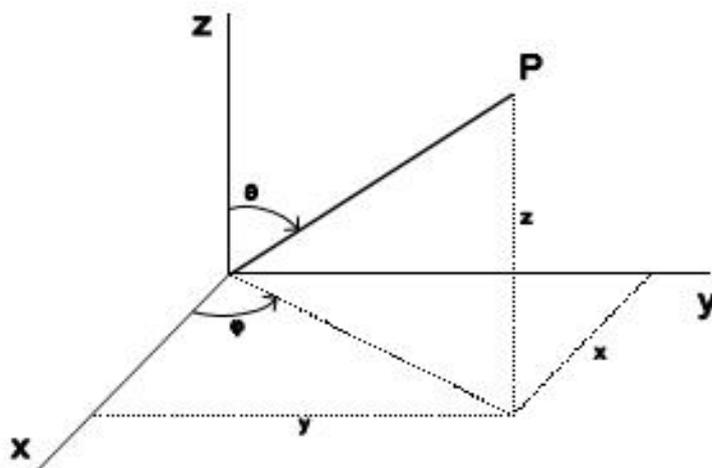
Solution

i.   The potential energy for the hydrogen atom can be written as,

$$V = \frac{-e^2}{4\pi\varepsilon_0 r}$$

The expression does not contain the Cartesian coordinate (i.e. xyz) but r which is a spherical polar coordinate.

ii.   The task of simplifying the therefore entails, conversion of the Cartesian coordinate to the polar coordinate. While the Cartesian coordinate deals with xyz, the polar coordinate in this case will also involves three parameters, namely, r, ϕ and θ. The relationship between r and the Cartesian system can be written as,

$$r^2 = x^2 + y^2 + z^2$$
$$r = \sqrt{x^2 + y^2 + z^2}$$

ii.   In spherical polar coordinates, r is the length of the radius vector from the origin to a point (xyz). In order to present analytical solution, let us consider a system involving both the polar and the Cartesian coordinate as shown in Fig. 2.6,

The angle between the z axis and the radius is θ while the angle between projection of the radius vector onto the xy plane and the +x axis is given as φ, From the diagram,

$$cos\theta = \frac{z}{r} = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$
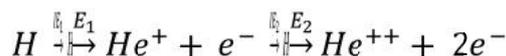
$$\theta = Cos^{-1}\frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$tan\varphi = \frac{y}{x}$$

$$\varphi = tan^{-1}\frac{y}{x}$$

Consequently, $\quad x = r\sin\theta cos\varphi, \quad y = r\sin\theta\sin\varphi$ and $z = rcos\theta/$
The Schrödinger equation can be written as,

3.8.3 Theory of bonding in helium atom

Helium atom has atomic number of two (Z = 2) and a mass of 4. The Bohr's theory fails to solve problems be young the hydrogen atom. However, it has been found that the approximation method gives solution that significantly agrees with experimental data. We can consider ground and excited state of helium as follows,

$$H \xrightarrow{E_1} He^+ + e^- \xrightarrow{E_2} He^{++} + 2e^-$$

IE_1 is the minimum energy required to remove one electron from helium atom in its ground state (i.e. first ionization energy). It is numerically equal to 25.49 eV. The second ionization energy may be calculated using the following equation.

$$IE_2 = -E_{1s}(H^+) = \frac{Z^2}{2n^2} = 2\,Hatree = 54.42\,eV$$

By definition, the ground state energy of helium atom can be calculated using the following equation,

$$E_0 = -(IE_1 + IE_2) = -79.02\,eV = 2.90372\,Hatree$$

The Schrodinger equation for the helium atom can be written as,

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\psi(r_1, r_2) = E\,\psi(r_1, r_2)$$

The first term in the Hamiltonian expression is the kinetic energy of electron 1, the second is the kinetic energy of electron 2, the third is the nuclear attraction of electron 1 and 2 and the last is the repulsive interaction between the two electrons. Finding exact solution for helium atom problem is complicated by the repulsive interaction term (i.e. $1/r_{12}$). Therefore, in order to solve the Schrodinger equation for the ground state helium atom, the problem is solved with the other terms (excluding the repulsive term). This approach is called neglect of electron repulsion. After solving, the last term is re-introduced. The

variables, r_1 and r_2 can be separated for the helium atom such that it will take the form of two separate hydrogen like atom wave function as follows,

$$Œ(r_1, r_2) = Œ_{1s}(r_1)\psi_{1s}(r_2) = e^{-Z(r_1 + r_2)}$$

The ground state energy of helium atom obtained from the above equation can be calculated from the equation, $2 \times \left(\dfrac{Z^2}{2}\right)$. This gives a theoretical value of -4 Hatree s opposed to the experimental value of - 2.90 Hatree. Thus, neglect of electron repulsion can introduce a very large error. This error can be reduced by using a functional form of the wave function, which replaces Z with adjustable parameter, . The new equation now becomes,

$$\overline{\psi}(r_1, r_2) = \overline{\psi}_{1s}(r_1)\psi_{1s}(r_2) = e^{-\alpha(r_1 + r_2)}$$

If the above function is used in the variational equation, we have,

$$\bar{E} = \frac{\int \bar{\psi}_{1s}(r_1)\psi_{1s}(r_2)H\psi_{1s}(r_1)\widehat{\psi_{1s}}(r_2)dr_1 r_2}{\int \bar{\psi}_{1s}(r_1)\psi_{1s}(r_2)\psi_{1s}(r_1)\widehat{\psi_{1s}}(r_2)dr_1 dr_2}$$

The Hamiltonian in the equation is the full Hamiltonian, which include the repulsive term $(1/r_{12})$. Consequently, the expectation value of the first part of the Hamiltonian generates the following expression,

$$\langle -\frac{1}{2}\nabla_1^2 \rangle = -\frac{1}{2} \, {}^2_2\rangle = \frac{\alpha^2}{2}$$

$$\frac{Z}{r_1}\rangle = \frac{Z}{r_2}\rangle = Z\alpha, \langle\frac{1}{r_{12}}\rangle = \frac{5}{8}\alpha$$

The variational energy is obtained by summing all the integers in the above equation as follows,

$$E_{(\alpha)} = \alpha^2 + 2Z\alpha + \frac{5}{8}\alpha$$

In order to account for the upper bound, we must find the optimal value of α, which minimise the variational energy. This is done by differentiating the above expression with respect to α. This gives,

$$\frac{d\bar{E}}{d\alpha} = 2\alpha + 2Z + \frac{5}{8}$$

From the above, the optimum value of the above parameter is obtained when $\frac{d\bar{E}}{d\alpha} = 0$, consequently,

$$2\alpha + 2Z + \frac{5}{8} = 0$$

$$\alpha = \left(Z - \frac{5}{16}\right)$$

Hence,

$$E_{(\alpha)} = \alpha^2 + 2Z\alpha + \frac{5}{8}\alpha = \left(Z - \frac{5}{16}\right)^2 + 2Z\left(Z - \frac{5}{16}\right) + \frac{5}{8}\left(Z - \frac{5}{16}\right)$$

$$E_{(\alpha)} = \left(Z - \frac{5}{16}\right)\left[\left(Z - \frac{5}{16}\right) + 2Z + \frac{5}{8}\right]$$

Since $2\alpha + 2Z + \frac{5}{8} = 0$, $2Z + \frac{5}{8} = 2\alpha$. Hence the above equation simplifies t0

$$E_{(\alpha)} = \left(Z - \frac{5}{16}\right)\left[\left(Z - \frac{5}{16}\right) - 2\alpha\right]$$

$$E_{(\alpha)} = \left(Z - \frac{5}{16}\right)\left[\left(Z - \frac{5}{16}\right) - 2\left(Z - \frac{5}{16}\right)\right]$$

$$E_{(\alpha)} = \left(Z - \frac{5}{16}\right)\left[-\left(Z - \frac{5}{16}\right)\right]$$

$$E_{(\alpha)} = -\left(Z - \frac{5}{16}\right)^2$$

The variational energy obtained from the above equation is numerically equal to -2.84775 Hatree, while the experimental value is -2.90572 Hatree. This is a good approximation with an error margin of only 2%. Other methods that have been found useful for approximating the ground state energy of helium atom are presented in Table 1.

Table 2.1: Estimated theoretical ground state energy of helium atom

Wavefunctions	Parameters	Energy
functions $e=Z(r_1+r_2)$	$Z = 2$	-2.75
functions $e=Z(r_1+r_2)$ $e=\alpha(r_1+r_2)$	$= 1.6875$	-2.84765
$\psi(r_1)\psi(r_2)$	best $\psi(r)$	-2.86186
$\frac{\psi(r_1)\psi(r_2)}{e=\alpha(r_1+r_2)}(1 + cr_{12})$	best , c	-2.89112
Hyleraas (1929)	10 parameters	-2.90363
Pekeris (1959)	1078 parameters	-2.90372

Non-inclusion of the repulsion term variable (r_{12}) can lead to considerable error. The effect is called electron correlation. The method that uses the function, $\psi(r_1)\psi(r_2)$ is called self-consistent field method and does not include the repulsion term, hence it has considerably error. The fourth entry, containing a simple correction for correlation, gives a considerable improvement. Hylleraas (1929) extended this approach with a variational function of the form,

$$Œ(r_1, r_2, r_{12}) = e^{-\alpha(r_1+r_2)} \times polynomial\ lnr_1, r_2, r_3$$

As can be seen in the results, this method gives a strong agreement with experimental result.

(i)   Self-Assessment Exercise

1.   What are the similarities and differences between sigma and pi bond?
2.   Identify the number of sigma and pi bond in HCN
3.   What is the significant hybridization in valence bond theory?
4.   A molecule with the formula AB_3 could have one of two different shapes. Give the shape and the hybridization of the central A atom for each.
5.   Use the following equation to calculate the ground state vibrational energy of helium, $E_{(\alpha)} = -\left(Z - \frac{5}{16}\right)^2$. Compare your results with experimental value and state the error margin.
6.   Write ionization equation for helium. Hence define the first ionization energy of helium. If the first ionization energy of helium is 25.49 eV, calculate the second ionization energy and the ground state energy of helium.
7.   Write the Schrodinger equation for helium atom and define all the terms in the equation. Which of the term can complicate the solution to the helium atom problem?
8.
a.   Write an expression for the probability density of linear combination of atomic orbital molecular orbital of a 1s σ-orbital. Hence, use the equation to deduced all the probabilities associated with the LCAO-MO.
b.   Write an expression for the probability density of linear combination of atomic orbital molecular orbital of a 1s σ*-orbital. Hence, use the equation to deduced all the probabilities associated with the LCAO-MO

Answer to Self-Assessment Exercise

1.   Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. Differences: bonds are stronger and result from end-to-end overlap and all single bonds are   bonds;   bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more   bonds (in addition to a   bond).
2.   HCN has two   (H–C and C–N) and two   (making the CN triple bond).
3.   Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.
4.   trigonal planar, sp^2; trigonal pyramidal (one lone pair on A) sp^3

5.   The variational energy obtained from the above equation is numerically equal to -2.84775 Hatree, while the experimental value is -2.90572 Hatree. This is a good approximation with an error margin of only 2%.

6.   The equation for ionization of helium is $H \xrightarrow{E_1} He^+ + e^- \xrightarrow{E_2} He^{++} + 2e^-$

IE$_1$ is the minimum energy required to remove one electron from helium atom in its ground state (i.e. first ionization energy). It is numerically equal to 25.49 eV. The second ionization energy may be calculated using the following equation.

$$IE_2 = -E_{1s}(He^+) = \frac{Z^2}{2n^2} = 2\ Hatree = 54.42\ eV$$

By definition, the ground state energy of helium atom can be calculated using the following equation,

$$E_0 = -(IE_1 + IE_2) = -79.02\ eV = 2.90372\ Hatree$$

7.   The Schrodinger equation for the helium atom can be written as,

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\psi(r_1, r_2) = E\psi(r_1, r_2)$$

The first term in the Hamiltonian expression is the kinetic energy of electron 1, the second is the kinetic energy of electron 2, the third is the nuclear attraction of electron 1 and 2 and the last is the repulsive interaction between the two electrons. Finding exact solution for helium atom problem is complicated by the repulsive interaction term (i.e. $1/r_{12}$).

8.   a.   The 1s σ-orbital is a bonding molecular orbital. Therefore, the probability density of the LCAO-MO of a 1s σ-orbital can be written as,

$$|Œ|^2 = N^2\left[\psi_{(1S)}(A) + \psi_{(1S)}(B)\right]^2 \qquad 1$$
$$= N^2\left[\psi_{(1S)}(A)^2 + \psi_{(1S)}(B)^2 + 2\psi_{(1S)}(A)\psi_{(1S)}(B)\right] \qquad 2$$

Equation 2 has three components which can be explained as follows.

  i. $Œ_{(1S)}(A)^2$, which represent the probability density of electron confined to the orbital, A.
  ii. $Œ_{(1S)}(B)^2$, which represents the probability density of electron confined to the orbital, B.
  iii. $2Œ_{(1S)}(A)\psi_{(1S)}(B)$, which is the extra contribution to the density of electron and is called overlap density.

The overlap density also represents an enhancement of the probability of finding electrons in the internuclear region above what it would be if they were confined to one of the two atoms.

b.   The 1s σ*-orbital is an antibonding molecular orbital, therefore the LCOA-MO for this system is

$$Œ' = N[\psi_{(1S)}(A) - \psi_{(1S)}(B)] \qquad 3$$

LCAO-MO for the above wave function correspond to a molecular orbital having energy higher than any of the contributing orbitals. Therefore, antibonding molecular orbital increases the energy of a system Whereas bonding molecular orbital is associated with constructive interferences, antibonding molecular orbital is associated with destructive interference. The probability function of antibonding molecular orbital can also be derived as it was done for bonding molecular orbital, hence we have

$$|Œ'|^2 = N^2\left[\psi_{(1S)}(A) - \psi_{(1S)}(B)\right]^2 \qquad 4$$
$$= N^2\left[\psi_{(1S)}(A)^2 + \psi_{(1S)}(B)^2 - 2\psi_{(1S)}(A)\psi_{(1S)}(B)\right]$$
$$5$$

It can be seen that the first two terms in equation 5 are the same as in those obtained for bonding molecular orbital and their significant is the same. However, the difference is in the sign of the third term, which is positive for bonding molecular orbital and negative for antibonding molecular orbital. The negative value (i.e. $[-2\psi_{(1S)}(A)\psi_{(1S)}(B)]$ clearly signify the factor that contribute to reduce the probability of finding electron between the nuclei.

4.0   CONCLUSION

Molecular orbital theory, hybridization and valance bond theories are the major theories that describes bonding in molecules. Although these theories have been widely applied to explain several binding, each of them is enveloped with some limitation indicating, a compromise for the best theory in explaining bonding in molecule depends on the nature of the molecule.

5.0   SUMMARY

A molecule is quite different from its constituent atoms and all the electrons belongs to the constituent atom and are considered to be moving under the influence of all nuclei.

Atomic orbitals of individual atoms combine to form molecular orbitals and these MOs are filled up in the same way as atomic orbitals are formed. In other words, Pauli's exclusion principle, Aufbau principle and Hund's rule of maximum multiplicity are followed. The molecular orbitals have definite energy levels and the shapes of MOs formed depend upon the shape of combining atomic orbitals.

Quantum chemistry can adequately predict the ground state energy of helium when the repulsion interact ion term is properly accounted for the right model

6.0   TUTOR MARKED ASSIGNMENT

(1)   Use appropriate theories to explain bonding in O_2, HCN and H_2 (6 minutes)
(2)   What are the advantage of molecular orbital theory over valence bond theory (4 minutes)

7.0   REFERENCES/FURTHER READINGS

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MODULE 2

UNIT 1 MOLECULAR SPECTROSCOPY

CONTENT

1.0   INTRODUCTION

Spectroscopy is the study of interaction of radiation with matter. Radiations relevant in spectroscopic study are those that belong to the electromagnetic spectrum. When any of the component of electromagnetic radiation (EMR) interact with matter, electron could be excited or the energy level of the molecule may change through interaction with proton. Generally, they are two basic types of spectroscopy, namely,

i.   **Atomic spectroscopy:** In atomic spectroscopic, all transitions are associated with changes in the configuration of electron.
ii.   **Molecular spectroscopy:** This is associated with changes in the energy of the molecule and is accompanied by changes in nuclei vibration and rotation.

Molecular spectroscopy is the study of the absorption or emission of electromagnetic radiation by molecules. Molecular spectroscopy can be classified based on the molecular energy that is been altered during absorption or emission. Consequently, we have rotational, vibrational and electronic spectroscopy. Rotational spectroscopy is concern with changes in rotational energy of a molecule. Vibrational spectroscopy deals with changes in vibrational energy of a molecule while electronic

spectroscopy is based on changes in the energy of a molecule due to different electronic arrangement or re-arrangement.

Internal energy of a molecule defines all the energies a molecule possesses. These include electronic (E_{el}), rotational (E_{rot}), translational (E_{tran}), vibrational (E_{vib}) and other forms of molecular energies (E_{others}). Therefore, we can write the total energy of a system as follows,

$$E = E_{Rot} + E_{Vib} + E_{Trans} + E_{El\ldots\ldots} + E_{Others}$$

In molecular spectroscopy, the significant components of the energy are rotational, vibrational and electronic energies because below 1000 K, all other components are negligible. This is consistent with the Born-Oppenheimer approximation, which account for a steady nucleus approximation. Therefore, according to this approximation, the total energy of a molecule can be written as,

$$E = E_{Rot} + E_{Vib} + E_{El} \qquad\qquad 3.1$$

Also, from Einstein theory, energy is related to frequency, i.e., $E = h\nu$. Therefore, rotational, vibrational and electronic energy terms are $h\epsilon_{Rot}$, $h\nu_{Vib}$ and $h\epsilon_{El}$ respectively. According to this approximation, the energy difference associated with excitation of electron ($h\bar{\nu}_{El}$) is much higher than the molecular vibrational energy ($h\nu_{Vib}$), which in turn is higher than molecular rotational energy ($h\epsilon_{Rot}$) because of the frequencies responsible for the respective transition. The general trend is,

$$h\epsilon_{El} > h\nu_{Vib} > h\epsilon_{Rot} \qquad\qquad 3.2$$

Transition between the vibrational energy levels is achieved by infra-red radiation, transition between rotational energy levels is achieved by far infra-red and by micro wave radiations while electronic energy levels transition is achieved by using visible light and ultra violet red radiations. Therefore, the major components of molecular spectroscopy are infra-red spectroscopy, UV-visible spectroscopy and micro wave spectroscopy. Vibrational transition results in changes in rotation of molecules while electronic transition results in changes in both vibration and rotation energies of a molecule.

There are also other significant spectroscopy techniques that can also be used to study molecules. These include nuclear magnetic spin resonance spectroscopy (NMR) and electron spin resonance spectroscopy (ESR). The energy levels that are studied under NMR and ESR spectroscopy are contrary to those studied under rotational, vibrational and electronic spectroscopy. NMR is based on changes in energy arising from different in orientation of certain nuclei due to the effect of applied magnetic field. These different orientations correspond to different energies. This enable radiation of suitable frequency to be used to study the energy

level separations. In ESR, differences in the orientation of a spinning electron correspond to different energy level and by using radiation of suitable frequency, the resulting energy separation can be studied.

The selection rule is a mathematical expression that can be used to know allowed or forbidden spectroscopic transition. According to the **time-dependent spectroscopic theory**, the probability of a molecule to absorb a light photon is given by the following expression,

$$W_{k \leftarrow 0} \; \alpha \; [\langle k|\mu_Z|0\rangle]^2 E_Z^2 \qquad\qquad 3.3$$

where $\langle k|\mu_Z|0\rangle$ is the matriz element of transition dipole moment. This factor is related to the Schrödinger wave equation according to the following equation,

$$\langle k|\mu_Z|0\rangle` = \int \varphi_k^* \mu_Z \varphi_0 dq \qquad\qquad 3.4$$

where φ_0 and φ_k^* are the molecular wave functions of the initial and excited states respectively. The total dipole moment is a vector which can be expressed as,

$$\overline{\mu} = \sum_i q_i \overline{r_i} \qquad\qquad 3.5$$

where q_i is the charge of the ith particle and r_i is the radius vector of the ith particle. The summation is done such that all particles are considered. From equations 3.4 and 3.5, it can be seen that the rate of transition is proportional to,

    i. E_Z^2 and hence the intensity of the incident light

    ii.   The square of the Z-component of the dipole moment matrix element, $\langle k|\mu_Z|0\rangle$

Equation 3.4 also reveals that the matrix element, $\langle k|\mu_Z|0\rangle$ depends on the symmetry of both the initial and excited molecular states, which in turn depends on the quantum number (vibrational or rotational quantum numbers, as the case maybe). Those quantum numbers that gives the matrix element a value of zero, presents molecular transition that is called forbidden transition. On the other hand, those transitions that results from quantum numbers that gives non zero values lead to allowed transition and hence transition selection rules.

In molecular spectroscopy, spectral lines originate from emission or absorption of light. In emission spectroscopy, a molecule returns from a higher energy level to a lower energy level and emits radiation. Absorption spectroscopy is concern with the absorption of monochromatic light that is a function of frequency. The **Bohr formula** can be used to presents the energies of the absorbed and emitted radiation according to equation 3.6,

$$h\epsilon = E_1 - E_2 \qquad\qquad 3.6$$

where ν is the frequency and h are the Planck constant. ν is related to the wavelength, λ according to the equation,

$$\lambda = \frac{c}{\nu} \qquad\qquad 3.7$$

where c is the speed of light. The reciprocal of the wave length is called wave number and can be written as,

$$\frac{1}{\lambda} = \bar{\nu} = \frac{\nu}{c} \qquad\qquad 3.8$$

Given that N_1 represent the population of the first level, i.e., level 1 and A_{12} is the Einstein coefficient of spontaneous emission, then applying the **Einstein theory of spontaneous radiation,** decay of excited state E_1 it can be stated that

$$\frac{dN_1}{dt} = -A_{12}.N_1 \qquad\qquad 3.9$$

Re-arranging and integrating equation 3.9, we have equation 3.10 and 3.11 respectively,

$$\int_{N_{1(0)}}^{N_{1(t)}} \frac{dN_1}{N_1} = -\int_0^t A_{12}dt \qquad\qquad 3.10$$

$$\ln\left(\frac{N_{1(t)}}{N_{1(0)}}\right) = -tA_{12} \qquad\qquad 3.11a$$

$$N_{1(t)} = N_{1(0)}e^{-tA_{12}} \qquad\qquad 3.11b$$

Generally, when monochromatic light passes through a sample, three possibilities are likely, namely, absorption, transmission, emission or scattering. The ratio of the transmitted light to the incident light (i.e. I/I_0) is called transmittance (T). According to Beer-Lambert law, the transmitted light intensity is a function of concentration of the specie (C) and of the sample path length (l). We can therefore express Beer-Lambert law as follow,

$$I = I_0e^{-kCl} \qquad\qquad 3.12$$

where k is the absorption cross section, C is the concentration and l are the path length. Most often, the unit of k is cm^2, C is in cm^3 and l is in cm. Since absorption, A is equal to $\log(I_o/I)$. The, Beer-Lambert law can be expressed according to equation 3.13,

$$\log\left(\frac{I_0}{I}\right) = A = \varepsilon lC \qquad\qquad 3.13$$

where ε is called molar absorptivity or extinction coefficient or molar concentration. Therefore, the relationship between absorbance and transmittance is given according to equation 3.14,

$$A = \log\left(\frac{1}{T}\right) \qquad\qquad 3.14$$

Since %transmittance is equal to transmittance x 100, equation 3.14 can also be written as

$$A = log\left(\frac{100}{\%T}\right) = 2 - log\left(\frac{1}{T}\right) \qquad\qquad 3.15$$

2.0   INTENDED LEARNING OUTCOME

When you have studied this session, you should be able to

- Understand the theory of spectroscopy, its origin and rules
- Understand the dipole moment, various types of dipole and dipole requirement for   transition and spectral observation
- Understand the theory of vibrational spectroscopy and explain the expansion of a chemical bond in terms of simple harmonic motion
- Know and apply the selection rule for vibrational spectroscopy
- Know the theory of rotational spectroscopy and derive equation for rotational energy based on the concept of rigid rotor   and centrifugal distortion.
- Derive and apply selection rule for rotational spectroscopy
- Understand the concept of electronic spectroscopy and its advantages over other spectroscopic techniques.
- Understand rovibrational spectroscopy and derive equation for   the combined pectroscopies

3.0   MAIN CONTENT

3.1   Dipole moment and interaction of radiation with matter

Spectroscopy employs electromagnetic radiation (including UV and visible range of radiation) to explored molecular properties. A consideration of a plane polarized (i.e. linear polarized light) indicates that it has both electric and magnetic components which are perpendicular to each other and can be described by the following equations

$$E_x = Asin(2\pi vt - kx)$$
$$H_y = Asin(2\pi vt - kx)$$

where E_x and H_y are strength of the oscillating electric and magnetic fields in the x and y directions respectively. The equation reveals that they are oscillating sinusoidally at a frequency of $2\pi v$ and since k is the same for both, the two are in phase. However, interaction of radiation with matter often occurs through electric component, hence the plane of polarization is the xy plane containing the direction of E and the propagation (see Fig. 3.1)
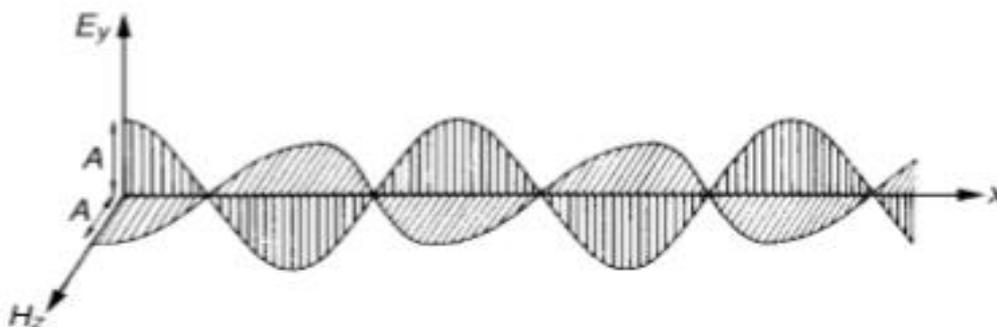
**Fig. 3.1: Plane polarized light travelling along the x-axis**

Stationary states are states that are time independent. If they are two states (state 1 and state 2), the pair may designate vibrational, rotational or electronic states. According to classical mechanics, the energy change when a system is subjected to radiation of frequency, v can be expressed as,

$$\Delta E = E_2 - E_1 = hv = hc\bar{v} \qquad\qquad 3.16$$

where $\bar{v} = \dfrac{1}{\lambda}$ and since $\lambda = c/v$, $1/\lambda = v/c$, hence $v = c\bar{v}$. When radiation interact with matter, the three things that are possible are induced absorption, spontaneous emission and induced or simulated emission (as shown in the diagram below)
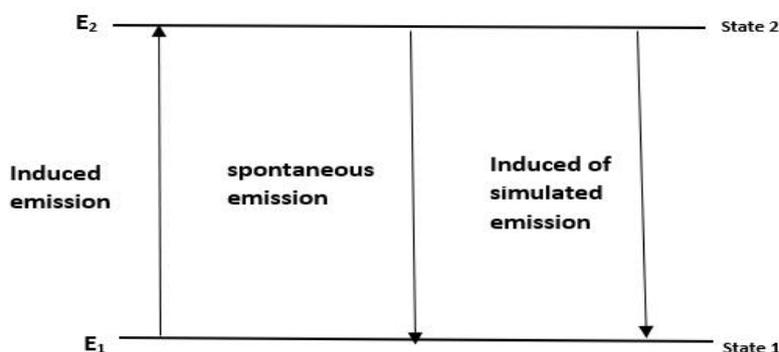
Induced absorption occurs when a molecule or atom absorbs radiation and move from state 1 to state 2, i.e. from lower energy level to higher energy level. This process can be represented as,

$$M + hc\bar{v} \rightarrow M^*$$
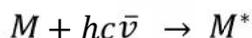
When the molecule or atom in the excited state (M*) emits radiation spontaneously, the process is called spontaneous emission, i.e.

$$M^* \rightarrow M + hc\bar{v}$$
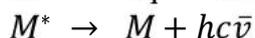
As shown in the two equations, spontaneous emission is the reverse of induced absorption indicating that the quantum of radiation absorbs is the same as the quantum of radiation emitted.

In stimulated or induced emission, a quantum of radiation is required to induced spontaneous emission of radiation by the excited molecule. This can be shown by the following equation,

$$M^* + hc\bar{v} \rightarrow M + 2hc\bar{v}$$

If the population in states 1 and 2 are N_1 and N_2, the rate of change of population due to induced absorption is given as,

$$\frac{dN_2}{dt} = N_1 B_{12}\, \rho(\bar{v}) \qquad\qquad 3.17$$

where B_{12} is the Einstein coefficient, $\rho(\bar{v})$ is the spectral radiation density and is given as,

$$\rho(\bar{v}) = \frac{8\pi}{\exp(hc v/kT)-1} \qquad\qquad 3.18$$

In the same way, induced emission changes the population by

$$\frac{dN_2}{dt} = -N_2 B_{21}\, \rho(\bar{v}) \qquad\qquad 3.18$$

B_{21} is the Einstein coefficient for the process. $B_{12} = B_{21}$. Consequently, the rate of change of the population N_2 gives spontaneous emission, which can be represented as,

$$\frac{dN_2}{dt} = -N_2 A_{21} \qquad\qquad 3.20$$

where A_{21} is another Einstein coefficient. It can be shown that if the population in the ground and excited states are the same, then

$$A_{21} = B_{21} 8\pi hc\bar{v}^3 \qquad\qquad 3.21$$

Equation 19 reveals that in induced emission, spontaneous emission increases as the wave number increases. It also reveals that the probabilities for stimulated absorption and emission are the same. Therefore, transition that has a high induced absorption will also has a high emission. The equation is very significant in laser design because Laser operates entirely on induced emission.

Dipole moment is a very serious parameter that govern the selection rule (i.e. allowed and forbidden transitions). For example, magnetic field can interact with magnetic moment and cause transition seen in electron spin spectroscopy and nuclear spin resonance spectroscopy, the oscillating electric field can interact with electric charges (i.e. positive charges from the nuclei and negative charge from electron cloud) and lead to transition in UV, atomic absorption and fluorescence spectroscopy. Another example is that for a molecule to be IR active, there must be a change in dipole moment as it vibrates when IR absorption occurs.

Finally, spectroscopy requires transition between energy states and not all transitions are possible. The change in dipole moment governs allowed transition. Dipole moment is defined as the summation of the product of charge and vector position for all charge particles. That is,

$$\mu_i = \sum_i q_i r_i \qquad\qquad 3.22$$

However, to evaluate the strength of interaction that cause transition, the dipole moment is called the transition dipole. It is interesting to state that absorption and emission cannot violates Pauli's exclusion principles, (which states that not more than two electrons can occupy a given orbital) indicating that there is some restriction to those transition that are possible or forbidden. The Einstein coefficients are related to the wave function of the ground and excited states (i.e. $Œ_1$ and ψ_2^* respectively) through the transition moment, R^{21}, by considering the quantum postulate relationship that link expectation in value of an observable (in this case, the transition dipole moment) with the wave functions. Therefore,

$$\boldsymbol{R^{21}} = \int Œ_2^* \mu_i \psi_1 \, \partial\tau \qquad\qquad 3.23$$

The transition probability is given by the square of the transition moment (R^{21}) and is related to the Einstein coefficient according to the following equation,

$$B_{21} = \frac{8\pi^3}{(4\pi\varepsilon_0)3h^2} |R^{21}|^2 \qquad\qquad 3.24$$

The transition probability, $|R^{21}|^2$ is also related to spectroscopy selection. Selection rules use the quantum numbers of the initial and final states to predict allow or forbidden transition. If the states do not satisfy the selection rules, then the electric-dipole transition rate will be zero. Transitions that obey the electric-dipole selection rules are called allowed transitions, while those which do not obey the rules are called forbidden transitions. Electric dipole allowed transitions have high transition probabilities and therefore have short radiative lifetimes, typically in the range 1–100 ns. Forbidden transitions, by contrast, are much slower. The different time-scales for allowed and forbidden transitions lead to another general classification of the spontaneous emission as fluorescence and phosphorescence, respectively. Fluorescence is a process in which the photon is emitted within a few nanoseconds after the atom has been excited, while phosphorescence gives rise to 'delayed' emission which persists for a substantial time.
In conclusion, selection rule for transition occurring through interaction with the electric vector of the radiation (i.e. electric dipole selection rule) is define as forbidden when $|R^{21}|^2 = 0$ but allowed when $|R^{21}|^2$ is non zero. It should be noted that non zero $|R^{21}|^2$ value can be found in some transition where the ground and the excited states have zero dipole

moment. For example, the transition from   to   * due to promotion of electron in ethylene. The figure below shows (a)   molecular orbital of ethylene (b)   * molecular orbital of ethylene

(a)   (b)
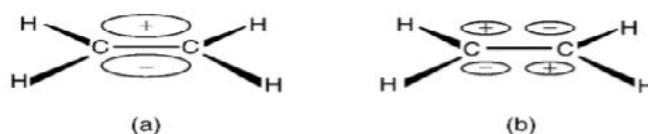
Fig. (a)   molecular orbital of ethylene (b)   * molecular orbital of ethylene

Therefore, non zero value of the transition moment, R^{21} can be observed in some molecules, even when the two states do not have permanent dipole moment.

Since the transition moment is a function of the dipole moment, its probabilities will also have components along the three coordinates. Therefore, we have,

$\mu_x = \sum_i q_i x_i, \ \mu_y = \sum_i q_i y_i$ and $\mu_z = \sum_i q_i z_i$

Consequently, the R^{21} will also have components in the x, y and z directions, which can be expressed as,

$R_x^{21} = \int \Psi_2^* \mu_x \psi_1$, $R_y^{21} = \int \Psi_2^* \mu_y \psi_1$ and $R_z^{21} = \int \Psi_2^* \mu_z \psi_1$

Consequently,

$$[R^{21}]^2 = (R_x^{21})^2 + (R_y^{21})^2 + (R_z^{21})^2$$

$$[R^{21}]^2 = \left\{ \int \Psi_2^* \mu_x \psi_1 \right\}^2 + \left\{ \int \psi_2^* \mu_y \psi_1 \right\}^2 + \left\{ \int \Psi_2^* \mu_z \psi_1 \right\}^2$$

3.25

Based on the number of interactions between radiation and light, radiative transition can be classified into electric dipole, magnetic dipole, electric quadrupole, magnetic quadrupole, electric octupole, etc. Characteristics of each of these transitions are shown in the Table 3.1.
Data presented in Table 3.1 reveals that the rate of transition decreases with increase in multipolarity (i.e. from dipole to quadrupole to octupole). Also evident from the results is that magnetic interaction becomes weaker by the same factor that the electric interaction increases. Consequently, electric dipole is the strongest transition by several order of magnitude indicating that other transitions are negligible.

Table 3.1: Classification and characterization of radiative transition based on multipolarity

Transition	Einstein coefficient, A (S^{-1})	Radiative life time (s)	Parity change
Electric dipole	$10^7 - 10^9$	1-100 ns	Yes
Magnetic dipole	10^3-10^5	0.01-1 ms	No
Electric quadrupole	10^3-10^5	0.01-1 ms	N0
Magnetic quadrupole	0.1 -10	0.1-10 s	Yes
Electric octupole	0.1-10	0.1-10 s	yes

Worked example 1

Calculate (i) the dipole moment for HCl given the following data, $r_H = (124.0,0,0), r_{Cl} = (-3.5, 0, 0), q_H = 2.70 \times 10^{-20}\ C$ and $q_{Cl} = 2.70 \times 10^{-20}\ C$. (ii)   Do you expect the transition moment to be equal to zero? Give reason for your answer.

Solution

The dipole moment in various directions are given as, $\mu_x = \sum_i q_i x_i$, $\mu_y = \sum_i q_i y_i$ and $\mu_z = \sum_i q_i z_i$. The total dipole moment is the sum of all the dipole moment from all direction. Therefore,

$$\mu_x = \sum_i q_i x_i$$
$$= [(2.70 \times 10^{-20}\ C)(124)$$
$$+ (-2.70 \times 10^{-20}\ C)(-3.5)]$$
$$= (334.8 + 9.5)\ 10^{-20} = 343.95 \times 10^{-20}$$
$$\mu_y = \sum_i q_i y_i = [(2.70 \times 10^{-20}\ C)(0) + (-2.70 \times 10^{-20}\ C)(0)]$$
$$= 0$$
$$\mu_z = \sum_i q_i z_i = (2.70 \times 10^{-20}\ C)(0) + (-2.70 \times 10^{-20}\ C)(0)$$
$$= 0$$

(i)   The total dipole moment is equal to
$$\mu = \mu_x + \mu_y + \mu_z = 343.95 \times 10^{-20} + 0 + 0$$
$$= 343.95 \times 10^{-20}\ Debye$$

The transition moment is given as $R^{21} = \int \psi_2^* \mu_i \psi_1\ \partial\tau$. Since the value of the dipole moment is non zero, then the integral will be non zero.

Worked example 2

Given the following data for hydrogen atom, show that hydrogen molecule cannot exhibit transition upon interaction with electromagnetic radiation. . $r_H = (124.0,0,0)$, $q_H = 2.70 \times 10^{-20} \, C$

Solution

The dipole moment of hydrogen molecule can be calculated as follows,

$$\mu_x = \sum_i q_i x_i$$
$$= [(2.70 \times 10^{-20} \, C)(124)$$
$$+ (-2.70 \times 10^{-20} \, C)(124)] = 0$$

Since the dipole moment is zero, the transition moment is also zero, hence there will be no transition when the molecule interacts with electromagnetic radiation because the square of the transition dipole moment is zero.

3.2   Vibrational spectroscopy

The development of Infra-red and Raman spectroscopy gave vibrational spectroscopy a wider range of application for almost all types of materials and in various physical states (gas, liquid and solid), especially for covalently bonded compound.

The compression and extension of a chemical bond can be treated in terms of the extension and compression of a spring, which obeys Hooke's law. According to Hooke's law, the restoring force (F_H) required to restore the spring to its original position (i.e., the restoring force is given by,

$$F_H = \frac{dV_{(x)}}{dx} = -k(r - r_{eq}) = -kx$$
3.25

where k is the force constant (the magnitude of the force constant determines the strength of the bond), $V_{(x)}$ is the potential energy and r is the internuclear distant, $r - r_{eq} = x$ The energy associated with this extension is given by,

Rearrangement of equation 16 and integration gives the value for the energy (i.e. potential energy ($V_{(x)} = E$) as follows,

$$dV_{(x)} = -kxdx$$

$$\int dV_{(x)} = -k \int xdx$$

$$E = \frac{1}{2}k(r - r_{eq})^2 \tag{3.26}$$

Equation 17 shows that the restoring force is proportional to the extension and that the energy is proportional to the square of the displacement. A system of this nature corresponds to the simple harmonic oscillator. Therefore, the model is known as a vibrating diatomic molecule model or the simple harmonic oscillator model. Although this model is an approximation, it forms the bases for analysing the vibrational spectra of molecules.

3.2.1 The simple harmonic oscillator

A plot developed from equation 16 will displayed a pattern shown in Fig. 3.2, that is a graph showing energy plotted against inter nuclear distant. The zero of the curves appears when the condition, $r = r_{eq}$ is fulfilled. Any energy in excess of the one obtained under this condition will originate from extension or compression of the bond.

The quantum mechanical Hamiltonian for a one-dimension simple harmonic oscillator is given as,

$$H = \frac{\hbar^2}{2\mu dx^2} + \frac{1}{2}kx^2 \tag{3.27}$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and is called the reduced mass of the system. Consequently, the Schrodinger equation for this system becomes,

$$\frac{d^2 \psi_{vib}}{dx^2} = \left(\frac{2\mu E_{vib}}{\hbar^2} - \frac{\mu k x^2}{\hbar^2}\right)\psi_{vib} = 0 \tag{3.28}$$

The solutions to the above equation are

$$E_{Vib} = \left(v + \frac{1}{2}\right)\hbar\omega_{osc} \tag{3.29}$$

$$\text{Œ}_{vib} = \left(\frac{1}{2^v v! \pi^{\frac{1}{2}}}\right)^{\frac{1}{2}} H_{vib}(y)exp\left(\frac{-y^2}{2}\right) \tag{3.30}$$

where v is the vibrational quantum number, $H_{vib}(y)$ is called Hermite polynomial and y is given as, $y = \left(\frac{4\pi^2 v\mu}{h}\right)^{1/2}(r - r_{eq})$ and ω_{osc} is the classical vibration frequency given as,

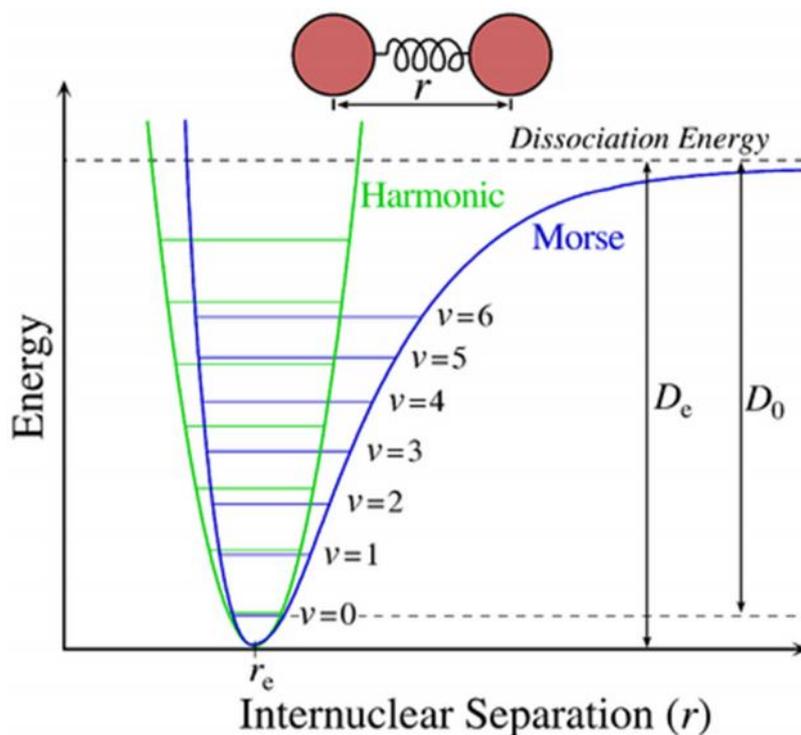$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{3.31}$$

Fig. 4.1: The Morse potential (blue) and harmonic oscillator potential (green).

(**Source**: https://en.wikipedia.org/wiki/Morse_potential)

Equation 3.31 reveals that the oscillating frequency increases with k (i.e. the stiffness of the bond but decreases with μ. The unit of the oscillation frequency in equation 19b is in Hertz (Hz). To convert this frequency to spectroscopic unit (i. e cms⁻¹), equation 19c is divided by c, the speed of light. This gives,

$$\overline{\omega_{osc}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad\qquad 3.32$$

Also, the vibrational energy can be expressed in spectroscopic unit by dividing equation 3.33 by hc and we have,

$$\epsilon_{Vib} = \frac{E_{Vib}}{hc} = \left(v + \frac{1}{2}\right)\overline{\omega_{osc}} \qquad\qquad 3.33$$

Equations 3.32 and 3.33 are expressions for the only energy allowed for simple harmonic oscillator. The vibrational quantum number (i.e. v) takes values of v = 0,1,2…….. Therefore, accordingly, the vibrational quantum number is equally spaced by $\overline{\omega_{osc}} = hc\omega_{osc}$. The lowest vibrational energy can be obtained from these equations when v = 0. The results are $E_{Vib} = \frac{1}{2}h\omega_{osc}$ (in Hz) or $\epsilon_{Vib} = \frac{1}{2}\overline{\omega_{osc}}$ (in cm⁻¹). This is the minimum energy a molecule may has, even at absolute zero temperature and is a consequence of uncertainty principle. Hence a

diatomic molecule (and other molecules) can not possess vibrational energy that is numerically equal to zero, indicating that the atoms can never be completely at rest with respect to each other. The value of the energy obtained under this condition is called zero-point vibrational energy ($\frac{1}{2}h\omega_{osc}$ or $\frac{1}{2}\overline{\omega_{osc}}$). The zero point vibrational energy is a function of the classical vibrational frequency, the strength of the chemical bond and on the atomic masses (Recall, $\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ or $\overline{\omega_{osc}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$). The concept of the zero-point vibrational energy draws a major line of distinction between classical mechanics and wave mechanics. Classically, the energy of a molecule can assume any integer values ranging from negative, zero and positive values. Quantum mechanically, the energy of a molecule is restricted to only certain permissible value. Therefore, wave mechanics insist that the vibrational energy of any molecule must have at least the minimum energy (i.e. the zero-point vibrational energy).

The selection rule for simple harmonic oscillator can be derived from the Schrödinger equation and without prove it can be stated as, $\Delta v = \pm 1$. This rule applies if the interaction of radiation with matter brings a change in the dipole moment of the molecule, which is possible for heteronuclear diatomic molecule. Homonuclear cannot be studied using vibrational spectroscopy because they have no dipole moment. M

As stated before, emission involves transition from higher level to lower level while absorption involves transition from lower level to higher level). If the selection rule is applied to the simplest transition involving emission (v+1→ v) and absorption, (v→ v+1), the results of the calculations are expressed in equation 20 and 21 for absorption and emission respectively,

$$\epsilon_{v\rightarrow v+1} = \left[(v + \tfrac{1}{2})\overline{\omega_{osc}}\right] - \left[(v + 1 + \tfrac{1}{2})\overline{\omega_{osc}}\right] = \left[\tfrac{2v+1}{2} - \tfrac{2v+3}{2}\right]\overline{\omega_{osc}} = - \overline{\omega_{osc}} \qquad 3.34$$

$$\epsilon_{v+1\rightarrow v} = \left[(v + 1 + \tfrac{1}{2})\overline{\omega_{osc}}\right] - \left[(v + \tfrac{1}{2})\overline{\omega_{osc}}\right] = \left[\tfrac{2v+3}{2} - \tfrac{2v+1}{2}\right]\overline{\omega_{osc}} = \overline{\omega_{osc}} \qquad 3.35$$

Equations 22 and 23 reveals that the amount of energy absorbed is equal to the amount emitted. This is true for any value of v. Therefore, there exist vibrational levels that are equally spaced because transition between two neighbouring states give rise to the same energy change. It is significant to state that the wave number of the spectral line absorbed or emitted is equal to the energy change. i.e., $\overline{v_{spect}} = \epsilon = \overline{\omega_{osc}}$. Therefore, a molecule absorbs radiation only if it can coherently interact

and it is only possible if it is the radiation of its own oscillating frequency.

Worked example 3

HCl shows a very intense absorption at 2886 cm⁻¹, a weak absorption at 5668 cm⁻¹ and a weaker absorption at 8347 cm⁻¹. Calculate the following

   (i)   The equilibrium frequency of absorption
   (ii)   The anharmonicity constant
   (iii)   The force constant ([Mass of H = 1.6727 amu, Mass of chlorine = 35.435 amu)]
   (iv)   The classical vibrational energy of the molecule if v = 2

Solution: Three set of equations can be generated for the fundamental absorption, first and second overtones as follows,

$$\overline{w_e}(1 - 2x_e) = 2886 \qquad\qquad 1$$
$$2\,\overline{w_e}(1 - 3x_e) = 5668 \qquad\qquad 2$$
$$3\,\overline{w_e}(1 - 4x_e) = 8347 \qquad\qquad 3$$

Expanding the brackets in equations 1, 2 and 3. We have equations 4, 5 and 6 respectively.

$$\overline{w_e} - 2x_e\overline{w_e} = 2886 \qquad\qquad 4$$
$$\overline{2w_e} - 6x_e\overline{w_e} = 5668 \qquad\qquad 5$$
$$\overline{3w_e} - 12x_e\overline{w_e} = 8347 \qquad\qquad 6$$

(i)   Equations 4, 5 and 6 can be solved simultaneously. This can be achieved by multiplying equation 4 by 3. Equation 4 + equation 5 – equation 6, element the meddle terms (i.e. $x_e\overline{w_e}$) and we have, $\overline{w_e} = 2989.50\ cm^{-1}$.

(II)   The value of the anharmonicity constant, x_e can be estimated by substituting for $\overline{w_e}$ in any of the equation. For example, for the second first overtone, Xe = 0.01739

(III)   The force constant can be solved by using the equation, $\overline{\omega_{osc}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ .Making k the subject of the equation, we have, $k = 4\pi^2\overline{\omega_{osc}}^2 c^2\mu = 516$ Nm⁻¹.

(IV)   The classical vibrational energy can be calculated using the equation, $\in_{Vib} = \left(v + \frac{1}{2}\right)\overline{\omega_{osc}}$, which gives 4484.25 cms⁻¹ (for v = 2)

3.3   Rotational spectroscopy

As a first approximation, the rigid rotor model can be used to study rotational motion of a molecule. Rigid rotor explains a rotation that proceeds without changes in distance. The total energy of a rigid rotor should consist of the sum of potential and kinetic energy. However, since the distance is fixed, the energy can be assumed to be dominantly kinetic, that is rotational energy and can be written as,

$$E_{Rot} = \frac{1}{2}\sum m_i v_i^2 \qquad\qquad 3.35$$

when m_i and v_i are the mass and the velocity of the rotating body. The linear velocity is related to the angular velocity according to the following equation,

$$\omega = \frac{v}{r}$$

Therefore, $v_i = \omega \times r_i$ and the rotational energy can be expressed as,

$$E_{Rot} = \frac{1}{2}\sum m_i v_i (\omega \times r_i) \qquad\qquad 3.36$$

The angular velocity is a scaler quantity hence the above equation can be simplified as follows,

$$E_{Rot} = \frac{\omega}{2}\sum m_i (v_i \times r_i) = \frac{\omega}{2}\sum l_i$$

$$E_{Rot} = \frac{\omega}{2}\sum l_i = \frac{L\omega}{2} \qquad\qquad 3.37$$

where l_i is the angular momentum of ith particle while L is the angular momentum of the entire system. If the moment of inertia is denoted as I, then $L = I\omega$. Therefore,

$$E_{Rot} = \frac{1}{2}I\omega^2$$
$$3.38$$

The above equation reveals that the energy of a rigid rotor increases with increase in angular frequency and with moment of inertia.

From the above, it can be inferred that the classical energy of a particle which rotates around an axis is given by $E = \frac{1}{2} I\omega^2$. where I is the moment of inertia and ω is the angular velocity in radian per second. The moment of inertia, I is a function of mass of the particle (m) and the radius of separation (r) and can be expressed as $I = mr^2$.

The number of axis through which rotation can occur is infinite and so the number of possible moments of inertia is also infinite. In order to overcome this problem, we introduce a second-rank tensor quantity (called the inertia tensor), which can be considered as an ellipsoid whose width in any direction is a measure of the corresponding moments of inertia.

The three principal axes of this ellipsoid are mutually perpendicular. One of them relates to the maximum possible moment of inertia (I_C), one to the minimum possible moment of inertia (I_A) and the other to the intermediate possible moment of inertia (I_B). Based on the relative values of their three principal moments of inertia, molecules can be classified into four major groups as presented in Table 1.

Table 1: Classification of molecules based on the relative values of their principal moment of inertia

Types of molecule	Property	Examples
Spherical top	$I_A = I_B = I_C$	CH_4, CCl_4 and SF_6
Symmetric top	$I_B = I_C \neq I_A$ and $I_A \neq 0$	
	(a) Prolate: $I_B = I_C > I_A$	CH_3I,
	(b) Oblate: $I_B = I_C < I_A$	BF_3, C_6H_6
Linear rotor	$I_A = 0$, $I_B = I_C$	CO_2, N_2O, C_2H_2
Asymmetric top	$I_A \neq I_B \neq I_C$	H_2O, C_2H_3Cl

Considering the above information, the classical rotational energy of an arbitrary object can be expressed as,

$$E_{Rot} = \frac{1}{2}I_A\omega_A^2 + \frac{1}{2}I_B\omega_B^2 + \frac{1}{2}I_C\omega_C^2 \qquad 3.39$$

where A, B and C are the principal axes of rotation

3.3.1 Angular momentum

Angular momentum can be analysed using classical and quantum mechanical approaches. Classically, angular momentum can take any value but quantum mechanically, angular momentum is restricted to certain permissible value, which is expressed in the equation 3.40,

$$p = \left(\frac{h}{2\pi}\right)\sqrt{J(J+1)} \qquad 3.40$$

where J is the rotational quantum number (which must be zero or positive), h is the Planck constant. In molecular spectroscopy, our concern is centered on possible changes in molecular energies and we can develop equation for allowed value of the molecular energy through classical approach. Classically, angular momentum is given as $p = I\omega_e$ (where I is the moment of inertia) but the rotational energy is ½ $I\omega^2$. Therefore,

$$E_{Rot} = \frac{I^2\omega^2}{2I} = \frac{p^2}{2I} \qquad 3.41$$

Substitution for p² in equation 3.41 (using equation 3.40), yields equation 3.42 and upon simplification, equation 33 is obtained.

$$E_{Rot} = \frac{\left[\left(\frac{h}{2\pi}\right)\sqrt{J(J+1)}\right]^2}{2I}$$
3.42

$$E_{Rot} = \frac{J(J+1)h^2}{8\pi^2 I}$$
3.43

In order to expressed the rotational energy in spectroscopic unit, we divide both sides of equation 3.43 by hc (where c is the speed of light). This gives

$$\epsilon_{Rot} = \frac{E_{Rot}}{hc} = \frac{J(J+1)h}{8c\pi^2 I} = BJ(J+1)$$
3.44

Equation 3.44 can be written as $\epsilon_{Rot} = BJ(J+1)$. $B = \frac{h}{8c\pi^2 I}$ and is called rotational constant expressed in cm⁻¹. The selection rule for the allowed transition is $\Delta J = \pm 1$. Let us consider the changes associated with some transitions as follows,

(i)   **J = 0 to J = 1**
$\Delta\epsilon_{Rot} = \epsilon_{J=1} - \epsilon_{J=0}$
$= 2B - 0 = 2B$

(ii)   **J = 1 to J = 2**
$\Delta\epsilon_{Rot} = \epsilon_{J=2} - \epsilon_{J=1}$
$= 2B(2+1) - B(1+1) = 4B$

(iii)   **J = 2 to J = 3**
$\Delta\epsilon_{Rot} = \epsilon_{J=3} - \epsilon_{J=2}$
$= 3B(3+1) - 2B(2+1) = 6B$

(iv)   **J = 3 to J = 4**
$\Delta\epsilon_{Rot} = \epsilon_{J=4} - \epsilon_{J=3}$
$= 4B(4+1) - 3B(3+1) = 8B$

Generally, for a transition from J to J+1 state, the change in rotational energy will be B(J+1)(J+2) – BJ(J+1) = (BJ² + 3BJ + 2B) – (BJ² - B) = 2B(J+1). Therefore, rotational transition will be characterised by a stepwise raising of the rotational energy by a multiple of 2. This can be seen in Fig. 3.3. The diagram reveals that only J to J+1 transition is allowed. This is consistent with the selection rule, which give allowed transition to be $\Delta J = \pm 1$. The implication is that for absorption, the transition is from J to J+1 but for emission, spectral will only be produced when the transition is from J+1 to J. In both cases, the spacing between each spectral transition is 2B.
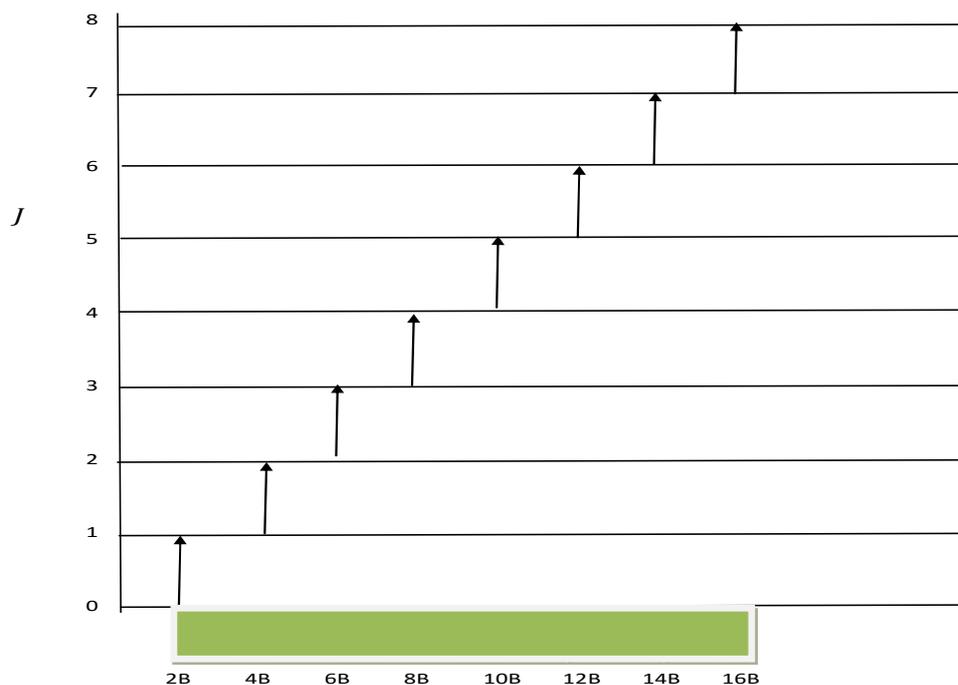
Fig. 3.3: Diagram showing allowed rotational transition

3.3.2 Centrifugal distortion: the semi-rigid body

A rotating molecule is not perfectly rigid. This means as the speed of rotation increases, the bond stretches (analogous to a case of swinging a weight attached to elastic in a circle) and leads to centrifugal distortion. This implies that equation 34 cannot be accurate in explaining the rotational energy of a real molecule. Therefore, we introduce a centrifugal distortion term to account for the rotation behaviour of a real molecule. Equation 34 is hereby amended to equations 35 (in Joules) and 33 (in spectroscopic unit, cm^{-1}).

$$E_{Rot} = \frac{h}{8\pi^2 cI}J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k}J^2(J+1)^2$$
$$3.45$$
$$\epsilon_{Rot} = \frac{E_{Rot}}{hc} = \frac{h}{8\pi^2 I}J(J+1) - \frac{h^3}{32\pi^4 I^2 r^2 kc}J^2(J+1)^2$$
$$3.46$$

Introducing rotation constants, B $= \dfrac{h}{8\pi^2 I}$ and D $= \dfrac{h^3}{32\pi^4 I^2 r^2 kc}$ we have the following equation

$$\epsilon_{Rot} = BJ(J+1) - DJ^2(J+1)^2 \qquad\qquad 3.47$$

84

Considering the rotational transition from level J to level J+1, in the presence of centrifugal distortion, we can calculate the allowed change in energy as follows,

$$\Delta\epsilon_{Rot} = \epsilon_{J=J+1} - \epsilon_J$$
$$= B(J+1)(J+2)] - D(J+1)^2(J+2)^2 - BJ(J+1) - DJ^2(J+1)^2$$
$$= B(J+1)(J+2)] - BJ(J+1) - D(J+1)^2(J+2)^2 - DJ^2(J+1)^2$$
$$= B(J^2 + 3J + 2 - J^2 - J) - D(J+1)^2(J^2 + 4J + 4 - J^2)$$
$$= B(2J+2) - D(J+1)^2(4J+4)$$
$$= 2B(J+1) - 4D(J+1)^3$$

Again if we ignore the centrifugal distortion, the change in rotational energy becomes 2B(J +1) as before. Therefore, lines on pure rotational spectrum is often equally spaced by 2B. However, if there is centrifugal distortion, the effective rotation constant B will depend on J and the lines will not be equally spaced but will occurs at positions defined by the equation, $2B(J+1) - 4D(J+1)^3$. The centrifugal distortion constant, D and frequency of oscillation are related according to equation 3.48,

$$D = \frac{4B^2}{\tilde{\Im}^2} = \frac{16\pi^2 B^2 c^2 \mu}{k}$$

     3.48

The force constant itself, $k = 4\check{S}^2\pi^2 c^2\mu$. Equations 3.42 to 3.44 apply to simple harmonic force field. The appropriate equation for the anharmonic force field will have more correction terms as expressed in equation 3.49,

$$\epsilon_{Rot} = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4$$

     3.49

Worked example 4

(a)   What is the differences and similarity between absorption and emission. Hence use the selection rule with respect to the simplest harmonic transition to show that the amount of energy associated with absorption is the same with that associated with emission.

(b)   With suitable equation, give reason to show that wave number of the spectral line absorbed or emitted is equal to the energy change.

(c)   Under what condition can a radiation absorbed by a molecule be effective?

(d)   Use the time independent spectroscopic theory to explain the likelihood of an absorption to lead to transition. What is the relationship between this theory and the Schrödinger equation?

(e)   Write an expression that defines molecular transition moment. Hence what are the factors that influence.

(f)   Use the matrix element associated with the time independent spectroscopy theory to explain forbidden transition and transition selection rule (i. e allowed transition).

Solution

(a) Emission involves transition from higher level to lower level while absorption involves transition from lower level to higher level). If the selection rules is applied to the simplest transition involving emission (v+1→ v) and absorption, (v→ v+1), the results of the calculations are expressed in equations1 and 2 for absorption and emission respectively,

$$\epsilon_{v \to v+1} = \left[(v + \tfrac{1}{2})\overline{\omega}_{osc}\right] - \left[(v + 1 + \tfrac{1}{2})\overline{\omega}_{osc}\right] = \left[\frac{2v+1}{2} - \frac{2v+3}{2}\right]\overline{\omega}_{osc} = -\overline{\omega}_{osc} \qquad 1$$

$$\epsilon_{v+1 \to v} = \left[(v + 1 + \tfrac{1}{2})\overline{\omega}_{osc}\right] - \left[(v + \tfrac{1}{2})\overline{\omega}_{osc}\right] = \left[\frac{2v+3}{2} - \frac{2v+1}{2}\right]\overline{\omega}_{osc} = \overline{\omega}_{osc} \qquad 2$$

Equations 1 and 2 reveal that the amount of energy absorbed is equal to the amount emitted. This is true for any value of v.

(b)   Therefore, there exist vibrational levels that are equally spaced because transition between two neighbouring states give rise to the same energy change. Therefore, the wave number of the spectral line absorbed or emitted is equal to the energy change. i.e, $\overline{v}_{spect} = \epsilon = \overline{\omega}_{osc}$.

(c)   A molecule absorbs radiation only if it can coherently interact and it is only possible if it is the radiation of its own oscillating frequency.

(d)   According to the time-dependent spectroscopic theory, the probability of a molecule to absorb a light photon is given by the following expression, $W_{k \leftarrow 0} \, \alpha \, [\langle k|\mu_Z|0\rangle]^2 E_Z^2$. where $[\langle k|\mu_Z|0\rangle]$ is the matriz element of transition dipole moment. This factor is related to the Schrödinger wave equation according to the following equation, $\langle k|\mu_Z|0\rangle = \int \varphi_k^* \mu_Z \varphi_0 dq$ where φ_0 and φ_k^* are the molecular wave functions of the initial and excited states respectively.

(e) The total dipole moment is a vector which can be expressed as, $\overline{\mu} = \sum_i q_i \overline{r_i}$ where q_i is the charge of the ith particle and r_i is the radius vector of the ith particle. The summation is done such that all particles are considered. From the time-dependent spectroscopic theory, it can be seen that the rate of transition is proportional to,

i. E_Z^2 and hence the intensity of the incident light
ii.   The square of the Z-component of the dipole moment matrix element, $\langle k|\mu_Z|0\rangle$

The time independent spectroscopy equation also reveals that the matrix element, $\langle k|\mu_Z|0\rangle$ depends on the symmetry of both the initial and excited molecular states, which in turn depends on the quantum number (vibrational or rotational quantum numbers, as the case maybe).

(f)   Those quantum numbers that gives the matrix element ($\langle k|\mu_Z|0\rangle$) a value of zero, presents molecular transition that is called forbidden transition. On the other hand, those transitions that results from quantum numbers that gives non zero values lead to transition selection rules, which signifies allowed transition.

Worked example 5

(a)   What is the requirement for the production of pure rotational spectrum by a molecule. Hence emulate the different selection rules that are applicable to the production of pure rotational spectrum?
(b)   Under symmetry conditions, what are the point groups that are associated with the production of pure rotational spectra

Solution.

(a)   The basic requirement for the production of pure rotational spectra is that there should be an oscillating dipole associated with molecular rotation. This implies that the molecule must have a permanent dipole moment indicating that the dipole moment must not be equal to zero, i.e $\mu \neq 0$. This is the gross selection rule for micro wave and for pure rotational spectroscopy. The other selection rule arises from allowed changes in angular momentum and is called the specific selection rule. This is given as $\Delta J = \pm 1$.
(b)   The only set of molecules that can have permanent dipole moment are molecules of the point group C_{nV} or C_n. Hence these molecules have rotational spectra.

Worked example 6

What is the formula for calculating the translational energy of a molecule? Hence why is the energy often considered as insignificant in molecular spectroscopy?

Solution

The translational energy of a molecule is similar to the energy of a particle in a three-dimensional box. This can be expressed as,

$$E_{(n_x, n_y, n_z)} = \frac{h^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

In general, the separation of the translational energy levels is many orders of magnitude smaller than the Boltzmann factor, *kT*, even for a box with dimensions on the order of molecular sizes. Therefore, translational behaviour of molecules is often treated under classical mechanics and not quantum mechanics, which is vital in molecular spectroscopy.

Worked example 7

(a)   Derive an expression for the classical and quantum rotational energy of a spherical top molecule

Solution

For a spherical top molecule, $I = I_A = I_B = I_C$. This means that the three principal axes of rotation are equal. The classical energy is given by,

$$E_{Rot} = \frac{1}{2}I_A\omega_A^2 + \frac{1}{2}I_B\omega_B^2 + \frac{1}{2}I_C\omega_C^2$$

Since $I_A = I_B = I_C = I$, the above equation becomes

$E_{Rot} = \frac{I}{2}(\omega_A^2 + \omega_B^2 + \omega_C^2)$.

But $P = I\omega$. $p^2 = I^2\omega^2$. Therefore, $E_{Rot} = \frac{I^2\omega^2 I}{2I} = \frac{p^2}{2I}$. Since P is quantized and $P = \left(\frac{h}{2\pi}\right)\sqrt{J(J+1)}$. Then the allowed rotational energy for the spherical top molecule is $E_{Rot} = \frac{h^2}{2\pi^2 I}\cdot J(J+1) = BJ(J+1)$

3.4   Rovibrational spectroscopy

As stated before, in molecular spectroscopy, the total energy of a molecule is the sum of contributions from electronic, vibrational and rotational energies. However, if we ignore the electronic energy (which is possible when we use electromagnetic frequency of low energy), then the total energy will be the sum of vibrational and rotational energy and can be expressed as follow,

$$\boldsymbol{E_{(v,J)}} = \left(v + \tfrac{1}{2}\right)\omega_e - \left(v + \tfrac{1}{2}\right)^2 x_e\omega_e + BJ(J+1) + DJ^2(J+1)^2$$
$$3.50$$

The absorption of energy equivalent to $E_{(v,J)}$ will lead to a transition. The absorbed energy that will initiate such a transition will correspond

to the infra-red spectroscopy. The gross selection rule for this transition is that a molecule must have a dipole moment that changes as it is vibrating. Mathematically, $d\mu/dt \neq 0$. The specific selection rules for real vibration is $\Delta v = \pm1, \pm2$ and ±3. In most cases, a change in the vibrational quantum number will be accompanied by a change in the rotational quantum number, J, under the selection rule, $\Delta J = 0, \pm1$. The study of a system of this nature that is characterised by both vibrational and rotational changes is called vibrotational or rovibrational spectroscopy. Vibrotational transitions often leads to the production of vibrotational bands, consisting of P, Q and R bands.

3.5   Electronic spectroscopy

According to the Born-Oppenheimer approximation, the energy of a molecule can be considered to be the sum of vibrational, rotational and electronic energies. Hence,

$$E = E_{Rot} + E_{Vib} + E_{El}$$
3.51

This implies that the change in energy can be expressed as,

$$\Delta E = \Delta E_{Rot} + \Delta E_{Vib} + \Delta E_{El}$$
3.52

For rotational spectra to occur, the molecule must have a permanent dipole, vibrational spectra occurs when the dipole of the molecule changes during vibration. However, electronic spectra can be produced for all molecules because changes in the distribution of electrons in a molecule is always associated by a change in the dipole moment of the molecule. This gives electronic spectroscopy, an edge over vibrational or rotational spectroscopy. For example, homo nuclear molecules such as H_2, N_2 and O_2 do not show rotation or vibration spectra but they do show electronic spectrum, from which vibration and rotation parameters can be obtained. Extension of equation 48 gives equation 3.53 for anharmonic and rigid rotor.

$$E_{Tot} = E_{El} + \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 x_e\omega_e + BJ(J+1) + DJ^2(J+1)^2 \quad 3.53$$

If we ignore the contribution from molecular rotation, equation 50 changes to equation 3.54,

$$E_{Tot} = E_{El} + \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 x_e\omega_e$$
3.54

Self Assessment Exercise

1.   Given that N_1 represent the population of the first level, i.e. level 1 and A_{12} is the Einstein coefficient of spontaneous emission, show that N_1 has an exponential relationship with A_{12}

2.   State at least one example of spectroscopic techniques that employs transition in vibrational, rotational and Electronic transition.

3.   (a)   What is selection rule in spectroscopy. Hence present an equation that gives the probability of spectroscopic transition

        (b)   What is the relationship between the wave function and the probability stated above ?

        (c)   What are the factors that affects the rate of transition and the magnitude of the matrix element

        (d)   What is the relationship between the value of transition matrix element and probability of transition

4.   (a)   Define what is dipole moment and transition dipole moment

        (b)   What is the relationship between the wave function and transition dipole moment?

        (c)   What is the relationship between transition dipole moment and the transition probability?

5.   Based on electric dipole moment, differentiate between allowed and forbidden transition

6.   Explain why ethylene exhibit non zero transition probability even if it does not have a permanent dipole moment.

7.   The selection rule for the allowed transition is $\Delta J = \pm 1$. Calculate the changes expected when the following transition occurs, (i) J= 0 to J =1, (ii)   J = 1 to J = 2, (iii) J = 2 to J = 4 (iv) J =3 to J = 4

8.   What are the shortcoming of rotational and vibrational spectroscopy over electronic spectroscopy

Answers to Self Assessment Exercise

1.   Applying the **Einstein theory of spontaneous radiation,** decay of excited state E_1 it can be stated that

$$\frac{dN_1}{dt} = -A_{12}.N_1 \qquad\qquad 1$$

Re-arranging and integrating equation 1, we have equation 3.10 and 3.11 respectively,

$$\int_{N_{1(0)}}^{N_{1(t)}} \frac{dN_1}{N_1} = -\int_0^t A_{12}dt \qquad\qquad 2$$

$$\ln\left(\frac{N_{1(t)}}{N_{1(0)}}\right) = -tA_{12} \qquad\qquad 3$$

$$N_{1(t)} = N_{1(0)}e^{-tA_{12}} \qquad\qquad 4$$

2.   Transition between the vibrational energy levels is achieved by infra-red radiation, transition between rotational energy levels is achieved by far infra-red and by micro wave radiations while electronic energy levels transition is achieved by using visible light and ultra violet red radiations

3.   The selection rule is a mathematical expression that can be used to know allowed or forbidden spectroscopic transition. According to the **time-dependent spectroscopic theory**, the probability of a molecule to absorb a light photon is given by the following expression,

$$W_{k\leftarrow 0}\; \alpha\; [\langle k|\mu_z|0\rangle]^2 E_z^2$$

where $\langle k|\mu_z|0\rangle$ is the matriz element of transition dipole moment. This factor is related to the

(b)   Schrödinger wave equation according to the following equation,

$$\langle k|\mu_z|0\rangle` = \int \varphi_k^* \mu_z \varphi_0 dq \qquad\qquad 1$$

where φ_0 and φ_k^* are the molecular wave functions of the initial and excited states respectively. The total dipole moment is a vector which can be expressed as,

$$\overline{\mu} = \Sigma_i\, q_i \overline{r_i} \qquad\qquad\qquad 2$$

where q_i is the charge of the ith particle and r_i is the radius vector of the ith particle. The summation is done such that all particles are considered.

(c)   From equations 1 and 2, it can be seen that the rate of transition is proportional to,

  iii. E_z^2 and hence the intensity of the incident light
  iv.   The square of the Z-component of the dipole moment matrix element, $\langle k|\mu_z|0\rangle$

Equation 1 also reveals that the matrix element, $\langle k|\mu_z|0\rangle$ depends on the symmetry of both the initial and excited molecular states, which in turn depends on the quantum number (vibrational or rotational quantum numbers, as the case maybe).

(d)   Those quantum numbers that gives the matrix element a value of zero, presents molecular transition that is called forbidden transition. On the other hand, those transitions that results from

quantum numbers that gives non zero values lead to allowed transition and hence transition selection rules.

4.   (a)   Dipole moment is defined as the summation of the product of charge and vector position for all charge particles. That is,

$$\mu_i = \sum_i q_i r_i$$

However, to evaluate the strength of interaction that cause transition, the dipole moment is called the transition dipole.

(b)   The Einstein coefficients are related to the wave function of the ground and excited states (i.e $Œ_1$ and ψ_2^* respectively) through the transition moment, R^{21}. This can be derived by considering the quantum postulate relationship that link expectation in value of an observable (in this case, the transition dipole moment) with the wave functions. Therefore,

$$\boldsymbol{R^{21}} = \int Œ_2^* \mu_i \psi_1 \, \partial\tau$$

(c)   The transition probability is given by the square of the transition moment (R^{21}) and is related to the Einstein coefficient according to the following equation,

$$B_{21} = \frac{8\pi^3}{(4\pi\varepsilon_0)3h^2} |R^{21}|^2$$

5.   Transitions that obey the electric-dipole selection rules are called allowed transitions, while those which do not obey the rules are called forbidden transitions. Electric dipole allowed transitions have high transition probabilities and therefore have short radiative lifetimes, typically in the range 1–100 ns. Forbidden transitions, by contrast, are much slower. Selection rule for transition occurring through interaction with the electric vector of the radiation (i.e electric dipole selection rule) is define as forbidden when $|R^{21}|^2 = 0$ but allowed when $|R^{21}|^2$ is non zero.

6.   It should be noted that non zero $|R^{21}|^2$ value can be found in some transition where the ground and the excited states have zero   dipole moment. For example, the transition from   to * due to promotion of electron in ethylene.   The figure below shows (a)   molecular orbital of ethylene (b)   * molecular orbital of ethylene

(a)   (b)
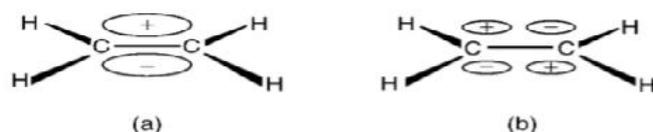
Fig. (a)   molecular orbital of ethylene (b)   * molecular orbital of ethylene

Therefore, non zero value of the transition moment, R^{21} can be observed in some molecules, even when the two states do not have permanent dipole moment.

7.   The selection rule for the allowed transition is $\Delta J = \pm 1$. The changes associated with some transitions as follows,

(v)   **J = 0 to J = 1**
$\Delta \epsilon_{Rot} = \epsilon_{J=1} - \epsilon_{J=0}$
$= 2B - 0 = 2B$

(vi)   **J = 1 to J = 2**
$\Delta \epsilon_{Rot} = \epsilon_{J=2} - \epsilon_{J=1}$
$= 2B(2+1) - B(1+1) = 4B$

(vii)   **J = 2 to J = 3**
$\Delta \epsilon_{Rot} = \epsilon_{J=3} - \epsilon_{J=2}$
$= 3B(3+1) - 2B(2+1) = 6B$

(viii) **J = 3 to J = 4**
$\Delta \epsilon_{Rot} = \epsilon_{J=4} - \epsilon_{J=3}$
$= 4B(4+1) - 3B(3+1) = 8B$

Generally, for a transition from J to J+1 state, the change in rotational energy will be $B(J+1)(J+2) - BJ(J+1) = (BJ^2 + 3BJ + 2B) - (BJ^2 - B) = 2B(J+1)$. Therefore, rotational transition will be characterised by a stepwise raising of the rotational energy by a multiple of 2.

1.   For rotational spectra to occur, the molecule must have a permanent dipole, vibrational spectra occur when the dipole of the molecule changes during vibration. However, electronic spectra can be produced for all molecules because changes in the distribution of electrons in a molecule is always associated by a change in the dipole moment of the molecule. This gives electronic spectroscopy, an edge over vibrational or rotational spectroscopy.

4.0   CONCLUSION

Spectroscopy deals with the study of interaction of radiation with matter. When radiation in form of photon strikes matter, several processes may be observed including, absorption, emission, molecular motions (vibration, rotation, electronic motions, etc).

5.0   SUMMARY

In order to obtained a spectrum that can give quality information, the interaction of radiation with matter must lead to appropriate selection rules.   They are three fundamental types of spectroscopy namely, vibrational spectroscopy (liken to simple harmonic oscillator and adjustment to anharminicity to suite real molecules), rotational spectroscopy (liken to Hook's law model and consequent amendment with rigid rotor model and centrifugal distortion) and electronic spectroscopy, which can be applied virtually to all types of matter.

6.0 TUTOR MARKED ASSIGNMENT

7.0   REFERENCES/FURTHER READINGS

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UNIT 2   COUPLING IN SPECTROSCOPY

CONTENT

1.0   INTRODUCTION

Observation of two bands of silver atoms Stern and Gerlach created disagreement with one of the principles of quantum mechanics because an angular momentum l is expected to give rise to $2l + 1$ orientations and can only be equal to 2 (i.e two bands) if $l = \frac{1}{2}$. This contradict the expectation that I must be an integer. This led to the findings that the observed angular momentum was not due to orbital angular momentum (the motion of an electron around the atomic nucleus) but from the motion of the electron about its own axis. This intrinsic angular momentum of electron, arising from its motion about its axis is called spin. Dirac further investigated spin angular momentum by combining quantum mechanics with special relativity and established the theory of relativistic quantum mechanics. Consequently, it was concluded that the spin of an electron about its own axis does not necessarily satisfy the same boundary conditions as those for a particle circulating around a central point, indicating that the quantum number for spin angular momentum is subject to different restrictions. In order to distinguish the spin angular momentum from orbital angular momentum, the spin quantum number s (in place of l and like l, s is a non-negative number) and m_s, the spin magnetic quantum number, for the projection on the z-axis. The magnitude of the spin angular momentum is $\{s(s + 1)\}^{\frac{1}{2}}\hbar$. The components, $m_s\hbar$ is restricted to the 2s+1 value with $m_s = s, s - 1, ... - s$.

Spin is an intrinsic property and for electron, only one value of s is allowed (i.e s = ½). Consequently, the magnitude of the spin angular

momentum for electron is, $\left\{\frac{1}{2}\left(\frac{1}{2}+1\right)\right\}^{\frac{1}{2}} = \left(\frac{3}{4}\right)^{\frac{1}{2}} \hbar.$ This gives $0.8660\hbar$ as the spin angular momentum. This means that the magnitude of the intrinsic spin angular momentum for an electron is $0.8660\hbar$ and is constant for all electrons. Consequently, the spin may lie in $2s+1 = 2(\frac{1}{2}) +1 = 2$ different orientation. One orientation correspond to $m_s = +\frac{1}{2}$ (usually represented as   or) and the other is $-\frac{1}{2}$ corresponding to   or . This does not violate Pauli's exclusion principle (which requires not more than two electrons to occupied a given orbital) and Aufbau principle which requires that the spin of electron must be opposed when two electrons occupy a given orbital. Proton and neutron also have $s = 1/2$, indicating that their spin angular momentum will be $0.8660\hbar$. The difference between these elementary particles is that because their masses is much heavier than electron, they will move at much slower rate than electron.

Some other particle (such as mesons) have spin value of 1 (i.e $s = 1$) indicating that their spin angular momentum would be $\{1(2+1)\}^{\frac{1}{2}}\hbar = 1.4142\hbar$. Photon is a spin-1 particle. It has zero rest mass, zero charge, energy (given as $h\nu$), linear momentum (given as $h/$ or $h\nu/c$), an intrinsic angular momentum of $1.4142\hbar$ and travel at the speed of light (i.e c).

Particles with half integer spin are called fermions while particles with integer spin are called bosons. Therefore, electrons and protons are fermions while photon is boson. It is worth stating that elementary particles that bind fermions together are bosons indicating that matter consist of assemblage of fermions held together by forces controlled by bosons.

Table 4.1 shows various quantum numbers, values and other properties. In the Table, the use of quantum numbers l and m_l points toward orbital angular momentum (circulation in space). s and m_s denote spin angular momentum (intrinsic angular momentum) while j and m_j are for a combination of orbital and spin momenta.
For many electron systems, upper case letters are used (i.e L, S, M_S, M_L, J, M_J, etc). Clebsh-Gordon series is used to combine two angular momenta. This is expressed as

$$j = j_1 + j_2, j_1 + j_2 - 2, \ldots\ldots [j_1 - j_2]$$

2.0   INTENDED LEARNING OUTCOMES

i.   Understand what is spin and the major contributors to spin
ii.   Differentiate between orbital and spin angular momenta
iii.   Identify the various quantum numbers related to angular momentum
iv.   Know what is coupling, spin-orbit coupling Russell-Saunders coupling and jj-   coupling and when they are most useful
v.   Solve mathematical problems associated with spin and coupling.

3.0   MAIN CONTENT

3.1   Spin Orbit Coupling

There are two contribution to angular momentum of an electron. One is a consequence of a magnetic moment that arises from its spin. The other contributor exists because an electron with orbital angular momentum (that is, an electron in an orbital with $l > 0$) behaves as a circulating current, and possesses a magnetic moment that arises from its orbital momentum. The interaction of the spin magnetic moment with the magnetic field arising from the orbital angular momentum is called spin–orbit coupling. The strength of the coupling, and its effect on the energy levels of the atom, depend on the relative orientations of the spin and orbital magnetic moments, hence on the relative orientations of the two angular momenta. The dependence of the spin–orbit interaction on the relative orientation of the spin and orbital momenta depends on the total angular momentum of the electron, the vector sum of its spin and orbital momenta. Consequently, when the spin and orbital angular momenta are nearly parallel, the total angular momentum is high but low when the two angular momenta are opposed.

Table 4.1: Properties of the angular momentum of electron

Quantum number	Symbol	Values	Specification
Orbital angular momentum	l	0, 1, 2,…..	$\{l(l+1)\}^{\frac{1}{2}}\hbar$ is the magnitude
Magnetic	m_l	$l, l-1,……-l$	component on z axis $= m_s\hbar$
Spin	s	½	$\{s(s+1)\}^{\frac{1}{2}}\hbar$ is the magnitude
Spin magnetic	m_s	$\pm\dfrac{1}{2}$	$\{s(s+1)\}^{\frac{1}{2}}\hbar$ is the magnitude
Total angular momentum	j	$l+s, \ l+s-1,..-j$	$\{j(j+1)\}^{\frac{1}{2}}\hbar$ is the

			magnitude
Total magnetic	$\overline{m_j}$		component on z axis = $m_l\hbar$

The total angular momentum of an electron is described by the quantum numbers j and m_j, with $j = l + \frac{1}{2}$ (when the two angular momenta are in the same direction) or $j = l - \frac{1}{2}$ (when they are opposed). The different values of j that can arise for a given value of l account for the levels of a term. For $l = 0$, the only permitted value is $j = -\frac{1}{2}$ ((the total angular momentum is the same as the spin angular momentum because there is no other source of angular momentum in the atom). When $l = 1$, j may be either $\frac{3}{2}$ (the spin and orbital angular momenta are in the same sense) or $\frac{1}{2}$ (the spin and angular momenta are in opposite senses).

The dependence of the spin–orbit interaction on the value of j is expressed in terms of the spin–orbit coupling constant, $\bar{A}$ (expressed as a wavenumber). For a given set of quantum numbers, s, l and j, the energy of the level can be expressed according to equation 4.1

$$E_{s,lj} = \frac{1}{2}hc\bar{A}\{j\,(j+1) - l(l+1) - s(s+1)\} \qquad\qquad 4.1$$

For example, the unpaired electron in the ground state of sodium atom has $l = 0$, so $j = \frac{1}{2}$. Because the orbital angular momentum is zero in this state, the spin–orbit coupling energy is zero (as is confirmed by setting j = s and $l = 0$). When the electron is excited to an orbital with $l = 1$, it has orbital angular momentum and can give rise to a magnetic field that interacts with its spin. Under this configuration, the electron can have j= $\frac{3}{2}$ or j =$\frac{1}{2}$, and the energies of these levels are

$$E_{s,lj} = \frac{1}{2}hc\bar{A}\left\{\frac{3}{2} \times \frac{5}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2}\right\} = \frac{1}{2}hc\bar{A}$$

$$E_{s,lj} = \frac{1}{2}hc\bar{A}\left\{\frac{1}{2} \times \frac{5}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2}\right\} = -hc\bar{A}$$

Another factor that affects the strength of spin-orbit coupling is the nuclear charge. The greater the nuclear charge, the greater the circulating current, and therefore the stronger the magnetic field. Since the spin magnetic moment of the electron interacts with this orbital magnetic field, the greater the nuclear charge, the stronger the spin–orbit interaction. It has been found that the coupling increases sharply with atomic number (as from Z=4). Whereas it is relatively small in H (giving rise to shifts of energy levels of no more than about 0.4 cm^{-1}), in

heavy atoms like Pb it is very large (giving shifts of the order of thousands of reciprocal centimetres).

3.1.1 Fine structure

Fine structure is the structure in a spectrum due to spin-orbit coupling. For example, two spectral lines are observed when the p electron of an electronically excited alkali metal atom undergoes a transition and falls into a lower s orbital. One line is due to a transition starting in a $j = \frac{3}{2}$ level and the other line is due to a transition starting in the $j = \frac{1}{2}$ level of the same configuration. The two lines are an example of the fine structure of a spectrum (the structure in a spectrum due to spin–orbit coupling). Fine structure can be clearly seen in the emission spectrum from sodium vapour excited by an electric discharge (for example, in one kind of street lighting). The yellow line at 589 nm (close to 17000 cm^{-1}) is actually a doublet composed of one line at 589.76 nm (16956.2 cm^{-1}) and another at 589.16 nm (16973.4 cm^{-1}); the components of this doublet are the 'D lines' of the spectrum. Therefore, in Na, the spin–orbit coupling affects the energies by about 17 cm^{-1}.

The total orbital angular momentum When several electrons are present, it is necessary to consider how their individual orbital angular momenta add together or oppose each other. The total orbital angular momentum quantum number, L, tells us the magnitude of the angular momentum through $\{L(L + 1)\}^{\frac{1}{2}}\hbar$. The number of orientation is 2L + 1, which is distinguished by the quantum number M_L. M_L can take the following values; L, L–1, ... , –L. Similar remarks apply to the total spin quantum number, S, and the quantum number M_S, and the total angular momentum quantum number, J, and the quantum number M_J. The value of L (a non-negative integer) is obtained by coupling the individual orbital angular momenta by using the Clebsch–Gordan series, which can be written as,

$$L = l_1 + l_2, \qquad l_1 + l_2 - 1, \ldots \ldots |l_1 - l_2|$$

The maximum value of $L = L_1 + L_2$ is observed when the two orbital momentum are in the same direction while the minimum value ($L = L_1 - L_2$) is observed when they are in opposite direction. $L = |L_1 - L_2|$ is an intermediate value and signified intermediate between the two.

Worked example 1

(i)   Calculate the value of L for 2p electrons
(ii)   What are the letters designated to L = 1, 2, 3,4 5 and 6?
(iii)   state the orbital terms the 2p electrons can give rise to.

(iv)   Why does a closed shell have zero angular momentum?

Solution

i.   For 20 electrons, $L_1 = L_2 = 1$ hence the maximum value is $L = l_1 + l_2 = 1 + 1 = 2$, the intermediate value is $L = l_1 - l_2 - 1 = 1 + 1 - 1 = 1$ while the minimum is $|l_1 - l_2| = |1 - 1| = 0$. Therefore, for 2p electrons, L = 2, 1, 0

ii.   When L = 1, 2, 3, 4, 5 and 6, they are designated the letters S, P, D, F, G, H and I respectively.

iii.   A p^2 configuration can give rise to D, P, and S terms. The terms differ in energy on account of the different spatial distribution of the electrons and the consequent differences in repulsion between them

iv.   A closed shell has zero orbital angular momentum because all the individual orbital angular momenta sum to zero.

3.1.2 The multiplicity

When there are several electrons to be taken into account, we must assess their total spin angular momentum quantum number, S (a non-negative integer or half integer) using Clebsh-Gordon series given as,

$$S = s_1 + s_2, \quad s_1 + s_2 - 1, \ldots\ldots |s_1 - s_2|$$

Electron has s = ½ which gives S = 1, 0 for two electrons (i.e $s_1 = s_2 = $ ½).

3.2 Russell–Saunders coupling scheme

The quantum number j provides information of the relative orientation of a spin of a single electron. However, when there are many electrons, J provides similar information. The presence of several electrons outside a closed shell (note, a closed shall has zero spin) requires consideration of the coupling of all the spins and all the orbital momenta. Problem arising from this, maybe complicated but can be simplified when the spin-orbit coupling is weak (mostly for atoms of low atomic number). The simplification is achieved by using the Russel-Saunders coupling scheme. The scheme is based on the observation that, if spin–orbit coupling is weak, then it is effective only when all the orbital momenta are operating cooperatively. Consequently, the coupling assumes that all the orbital angular momenta of the electrons couple to give a total L, and that all the spins are similarly coupled to give a total S. Hence the two momenta couples through the spin–orbit interaction to give a total J. The permitted values of J are given by the Clebsch–Gordan series, which can be written as,

$$J = L + S, L + S - 1, |L - S|$$

3.3   J-J coupling

Russell–Saunders coupling fails when the spin–orbit coupling is large (in heavy atoms, those with high Z). In order to overcome this shortcoming, the individual spin and orbital momenta of the electrons are coupled into individual j values; then these momenta are combined into a grand total, J. This scheme is called jj-coupling. If the spin and the orbital angular momentum of each electron are coupled together strongly, it is best to consider each electron as a particle with angular momentum j= or . These individual total momenta then couple as follows:

$j_1 = \dfrac{3}{2}$	and	$j_2 = \dfrac{3}{2}$	J = 3, 2, 1, 0
$j_1 = \dfrac{3}{2}$	and	$j_2 = \dfrac{1}{2}$	J = 2, 1
$j_1 = \dfrac{1}{2}$	and	$j_2 = \dfrac{3}{2}$	J = 2,1
$j_1 = \dfrac{1}{2}$	and	$j_2 = \dfrac{1}{2}$	J = 1, 0

(i)   Self Assessment Exercises

1.   When electron in sodium is excited to an orbital with $l = 1$, it has orbital angular momentum and can give rise to a magnetic field that interacts with its spin. Calculate the energies of the level, electron can have in terms of associated constant.

2.   (i)   Explain how observation of two bands in the spectrum of silver atoms disagrees with quantum mechanics and give reasons for the observation
     (ii)   Define the term, spin

3.   Calculate the magnitude of spin for the following particles (i) electron (ii) proton and neutron (iii) photon. How many orientations can the spin lies?

4.   In a single sentence, define what is spin orbit coupling. State two factors that influences the strength of spin orbit coupling,

5.   Use Clebsh-Gordon series to calculate the total spin of electron

6.   What is the better coupling method, that is more effective when the spin orbit coupling is weak? Hence define the preferred coupling rule.

7.   Under what condition will the Russel-Saunders coupling fails? Hence what is best coupling method when it fails?

Answer to Self Assessment Exercise

1.   Under the stated configuration, the electron can have $j = \frac{3}{2}$ or $j = \frac{1}{2}$, and the energies of these levels are

$$E_{s,lj} = \frac{1}{2} hc\bar{A} \left\{ \frac{3}{2} \times \frac{5}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2} \right\} = \frac{1}{2} hc\bar{A}$$

$$E_{s,lj} = \frac{1}{2} hc\bar{A} \left\{ \frac{1}{2} \times \frac{5}{2} - 1 \times 2 - \frac{1}{2} \times \frac{3}{2} \right\} = -hc\bar{A}$$

2.   (i)   Observation of two bands of silver atoms Stern and Gerlach created disagreement with one of the principles of quantum mechanics because an angular momentum l is expected to give rise to $2l + 1$ orientations and can only be equal to 2 (i.e two bands) if $l = \frac{1}{2}$. This contradict the expectation that I must be an integer. This lead to the findings that the observed angular momentum was not due to orbital angular momentum (the motion of an electron around the atomic nucleus) but from the motion of the electron about its own axis.

(ii)   This intrinsic angular momentum of electron, arising from its motion about its axis is called spin

3   The magnitude of the spin angular momentum is $\{s(s + 1)\}^{\frac{1}{2}}\hbar$.

   (i)   For electron, only one value of s is allowed (i.e s = ½). Consequently, the magnitude of the spin angular momentum for electron is, $\left\{ \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right\}^{\frac{1}{2}} = \left(\frac{3}{4} \right)^{\frac{1}{2}} \hbar$. This gives $0.8660\hbar$ as the spin angular momentum. Consequently, the spin may lie in $2s+1 = 2(\frac{1}{2}) +1 = 2$ different orientation

   (ii)   For proton and neutron, allowed value of s is also 1/2. Therefore, the magnitude of the spin angular momentum for electron is, $\left\{ \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right\}^{\frac{1}{2}} = \left(\frac{3}{4} \right)^{\frac{1}{2}} \hbar$. This gives $0.8660\hbar$ as the spin angular momentum. Consequently, the spin may also lie in $2s+1 = 2(\frac{1}{2}) +1 = 2$ different orientation

   (iii)   have spin value of 1 (i.e s = 1) indicating that their spin angular momentum would be $\{1(2 + 1)\}^{\frac{1}{2}}\hbar = 1.4142\hbar$. Consequently, the spin may lie in $2s+1 = 2(1)+1 = 3$ orientations.

4.   The interaction of the spin magnetic moment with the magnetic field arising from the   orbital angular momentum is called spin–orbit coupling. The strength of the coupling,   and   its effect on the energy levels of the atom, depend on

(i)   the relative orientations of the spin and orbital magnetic moments, hence on the relative   orientations of the two angular momenta

(ii)   The nuclear charge also influences spin orbit coupling. The greater the nuclear charge, the greater the circulating charges and the magnetic moment, hence the strength of the spin-orbit coupling.

5.   When there are several electrons to be taken into account, we must assess their total spin angular momentum quantum number, S (a non-negative integer or half integer) using Clebsh-Gordon series given as,

$$S = s_1 + s_2, \qquad s_1 + s_2 - 1, \ldots \ldots \ldots |s_1 - s_2|$$

Electron has s = ½ which gives, $S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} + \frac{1}{2} - 1, \ldots \ldots \ldots \left|\frac{1}{2} - \frac{1}{2}\right|$ and S = 1, 0 for two electron (i.e $s_1 = s_2 \equiv$ ½).

6.   when the spin-orbit coupling is weak (mostly for atoms of low atomic number). The simplification is achieved by using the Russel-Saunders coupling scheme. The scheme is based on the observation that, if spin–orbit coupling is weak, then it is effective only when all the orbital momenta are operating cooperatively.

7.   Russell–Saunders coupling fails when the spin–orbit coupling is large (in heavy atoms, those with high Z). In order to overcome this shortcoming, the individual spin and orbital momenta of the electrons are coupled into individual j values; then these momenta are combined into a grand total, J.

4.0   CONCLUSION

Electron can move around the nucleus and around its own axis. Hence electron has two set of angular momenta originating from orbital and spin. They are orbital angular momentum and spin angular momentum. Therefore, the total angular momentum is the sum of contribution from spin and orbital.

5.0   SUMMARY

The interaction of the spin magnetic moment with the magnetic field arising from the orbital angular momentum is called spin–orbit coupling. The strength of spin-spin coupling depends on the nuclear charge, level of orientation of spin moment and orbital magnetic moment. When the spin-spin coupling is weak, the prefer coupling is Russell-Saunders Coupling. However when the spin-spin coupling is high, Russell-Sauders coupling fail given gap for jj-coupling as the preferred coupling.

6.0   TUTOR MARKED ASSIGNMENT

1.   What are the conditions requires for applicability and failures of the following coupling
    (1)   J-J coupling   (5 minutes)
    (2)   Russell-Saunders   (5 minutes)

7.0   REFERENCES/FURTHER READINGS

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MODULE 3

UNIT 1   GROUP THEORY AND SYMMETRY

CONTENT

1.0   INTRODUCTION

A system is said to have symmetry if it has a mirror image, indicating that it will look the same if viewed in a mirror. The study of symmetry is essential in chemistry because through the mathematical framework known as group theory, it provides information that can be used to gain insight into some physical and chemical properties of a system. Group theory arises from classification of symmetry of molecule and it is a useful tool that can provide information on the following,

i.   Prediction of chirarity or polarity of a molecule
ii.   Examination of chemical bonding and visualization of molecular orbitals
iii.   Prediction of the ability of a molecule to absorb light of a given polarization and the associated spectroscopic transition
iv.   Investigation of vibrational motion of a molecule

In symmetry, operation is an action that render an object or a molecule indistinguishable (i.e. looking the same) after the action has been performed. For example, if we rotate water molecule at 180 ° about the axis that passes through the oxygen atom, it will look the same as the water molecule before the rotation was performed.
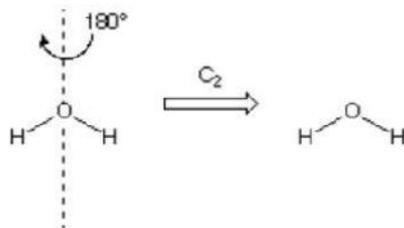
Fig. 5.1: Symmetry operation: Rotation of water at 180 Ê

Apart from rotation, there are different types of symmetry operations. However, each symmetry operation has a corresponding symmetry element, which is the axis, plane, line or point through which symmetry operation is carried out. When symmetry operation is carried out, all the point that constitute the symmetry element will not move but stayed in the same place throughout the symmetry operation. Some of these symmetry elements are

i.   Symmetry axis in rotation
ii.   Plane of symmetry in reflection
iii.   Centre of symmetry in inversion

2.0   INTENDED LEARNING OUTCOMES

When you have studied this session, you should be able to

- State what is symmetry
- Discuss what is symmetry elements and symmetry operations
- Carry out symmetry operations on some molecules
- discuss symmetry point group and group theory
- Classify symmetry groups to various classes
- Know the application of symmetry in chemistry

3.0   MAIN CONTENT

3.1   Symmetry Operation

The different types of symmetry operations that are possible in group theory are highlighted in this section.

3.1.1 Identity Operation.

Identity operation is often denoted as E. In identity operation, the molecule does not move and all the atoms of the molecule remain at the same position when identity operation is carried out. It is significant to state that all molecule has identity operation and can be achieved by

perfuming several operations, which finally returns the molecule to its original appearance. Fig. 5.2 shows how successive rotation of cyclopropane at 120 ° can produce an identity element, E
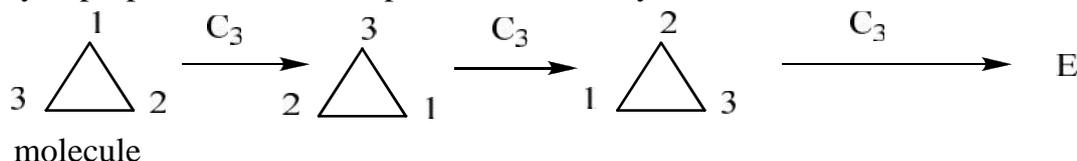
 molecule
Fig. 5.2: Symmetry operations in cyclopropane

In the above operation, rotation of the molecule through an angle of 120 ° (i.e C_3 operation) for three times, will bring back the original molecule. This implies that three C_3 rotation of the yields $C_3^3 = E$. Generally, for n axis of rotation, rotation for n times yields $C_n^n = E$

3.1.2 Proper Rotation

Proper rotation applied to an n-fold axis of rotation and describes rotation by 360 °/n such that the molecule will be left unchanged. The various angles that are associated with different rotation are shown in Table 5.1. It significant to note that rotation at 2 x (2 /6) gives $C_6^2 = C_3$, rotation at 3 x (2π/6) gives $C_6^3 = C_2$, rotation at 4 x (2 /6) gives $C_6^4 = C_3^2$, rotation at 5 x (2π/6) gives C_6^5 and rotation at 6(2 /6) gives $C_6^6 = E$. Generally, C_n operation generate n operations given by $C_n, C_n^2, C_n^3, C_n^4, C_n^5 \ldots and \ C_n^n (E)$. For example, ammonia which has C_3 axis. Proper rotation operation on ammonia will create three group namely, $C_3, C_3^2 \ and \ C_3^3 (E)$.

Table 5.1: Angles associated with some proper rotation symmetry

Symmetry operation	Angle of rotation in degree	Angle of rotation in radian
C_1	360	2
C_2	180	3 x (2 /6)
C_3	120	2 x (2 /6)
C_4	90	2 /4
C_5	72	2 /5
C_6	60	2 /6

3.1.3 Reflection

If reflection about a mirror plane gives the same molecule/object back then there is a plane of symmetry. Reflection can be achieved through three different types of plane. Reflection through vertical plane (v) contain the principle axis. Reflection through horizontal plane (h) are perpendicular to the principle axis while reflection through dihedral

planes ($_d$) contain the principle axis and bisect two C_2 axis. The different types of reflections are illustrated in the Fig. 5.3below,
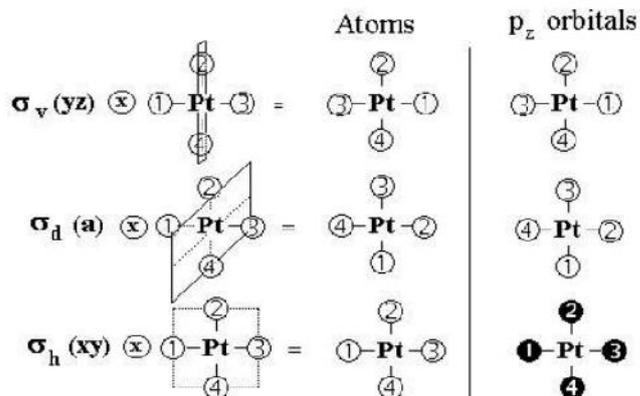

Fig. 5.3: Different types of reflections

When mirror plane is operated n times, we have ^{n}. This will give E if n is even and gives   when n is odd.

3.1.4 Improper Rotation

Improper rotation is a combination of two operations, proper rotation Cn and reflection,   . . Improper rotation is designated as S_n, which indicate n fold rotation, followed by reflection through the rotation axis. Example of improper rotation operation on methane is shown in Fig. 10 below
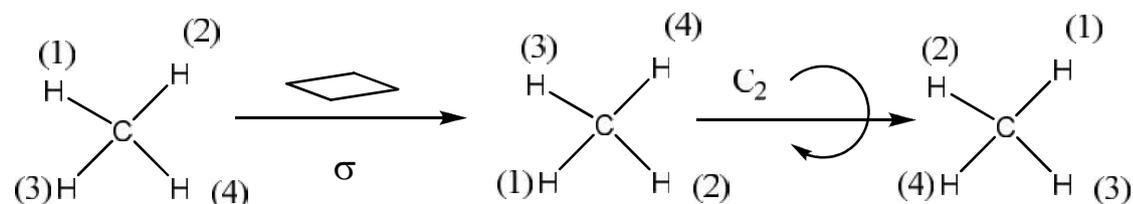
**Fig.5.4: Improper rotation (S_4) in methane**

3.1.5 Inversion

Inversion through the centre of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the centre of inversion and out to the same distance on the other side of the molecule. If a line drawn from one side of an atom in a molecule passes through the centre into the opposite side and produce equivalent point, then the operation is inversion. Fig. 11 below show inversion operation, i on XeF_4
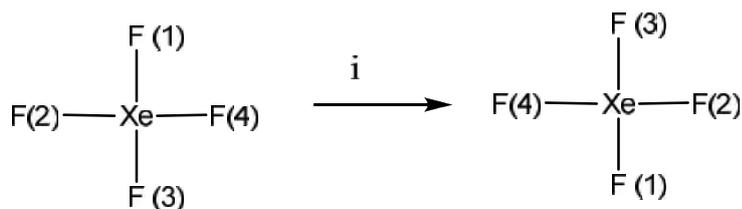
Fig. 5.5: Operation of inversion on XeF$_4$

3.2   Symmetry Point Group

All symmetry elements (lines, point or plane) will intersect at a given point. This makes it possible to classify molecules based on their symmetry. The collection of symmetry element present in a molecule is called point group. For example, the point group for water is C_{2v} and consist of identity element, E, two fold rotation axis, C_2 and two reflection planes, σ and σ*. The point group for a square molecule (such as tetraferric xenon and tetracynonickel are shown below (D_{4h})
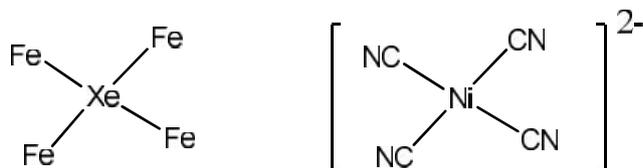
Hexagonal molecule such as benzene has the symbol, D_{6h}. The number indicate the order of the principal axis. The lower-case subscript, h indicates that there is n (equal to 6 for benzene) C_2 (nC_2) at right angle to the principal C_n axis.

Point group symmetry is widely used in spectroscopy, quantum and crystallography chemistry. An individual point group can be represented by a set of symmetry operations, which include,

  i.   E: The identity operation
 ii. C_n : rotation by 2 /n angle
iii. S_n : Improper rotation defined as the rotation at 2 /n angle followed by reflection in the plane perpendicular to the axis
iv.   σ$_h$: Horizontal reflection plane (perpendicular to the principal axis)
 v.   σ$_v$: Vertical reflection plane (contain the principal axis)
vi.   σ$_d$: Diagonal reflection plane (contain the principal axis and bisect the angle between two C_2 axes perpendicular to the principal axis) where n is an integer and the principal axis is the C_n axis with the largest value of n. A molecule is said to belong to a symmetry point group if it is unchanged under all the symmetry operations of the given group. Some properties of a molecule (such as vibrational, electronic and vibronic states, normal vibrational modes, orbital) may show similarity or

differences in behaviour under symmetry operations of the molecule point group. This behavior coincide with irreducible representation or irreducible character. All irreducible representations of the symmetry point groups may be found in the corresponding character table.

3.3   Classification of symmetric point group

Generally, symmetric point groups can be classified into the following classes,

3.3.1 Non-Axial Symmetries:

Non axial symmetries consist of C_1, C_i and C_s. C_1 has only one symmetric operation, which is E. This group has an order of 1, indicating that symmetric operations (except E) such as proper rotation, reflection, mirror and others cannot be carried out. Example of molecule in this class is HCFBrCl. C_i group has two symmetric operations (E, i) and an order of 2. Example of molecule in this group is $C_2H_2F_2Cl_2$, which has an inversion centre. C_s group has two symmetric operations (E, σ) and an order of 2. Example of molecule in C_s class is CH_2BrCl, which has a mirror plane.

3.3.2 Cyclic symmetries

This group consist of the cyclic group (C_n), the pyramidal group (C_{nv}) and the reflection group (C_{nh}) and the improper rotation group (S_n). Compounds in these classes have only one proper or improper rotation axis.

The cyclic group (C_n) has an order equal to n and defines a rotation through an angle of $2\pi/n$. The symmetry elements for C_n are $E, C_n^1, C_n^2, C_n^3, C_n^4 \ldots \ldots C_n^{n-1}$. Example of molecule in this class is $C_2H_4Cl_2$.

The pyramidal group is characterized by symmetric element, E, C_n and nσ and the symmetry operations are $E, C_n^k (k = 1, 2, 3 \ldots, n - 1)$ and $n\sigma_V$. The order of C_{nv} group is 2n. For example, ammonia belongs to C_{3v} group. It has C_3 (E, C_3^1, C_3^2) axis and three mirror planes, 3σ (i.e, σ_σ, σ_v' and σ_v'').

The reflection group (C_{nh}) has symmetry elements equal to E, C_n, σ_h and S_n. Therefore symmetry operation for this group will yield {E, C_n^k(k=1, … ,n-1), $_h$, $_hC_n^m$(m=1, … ,n-1)}. The order of C_{nh} group is 2n and $C_2H_2F_2$ is an example of a molecule in this group. This molecule has C_{2h} point group.

For the S_n group, n can only be, 4, 6, 8, 10…… and the symmetry elements are E and Sn while the symmetry operations are {E, Snk(k=1, … ,n-1)}. The order of Sn group is n. For example, the point group of 1,3,5,7 -tetrafluoracyclo octatetrane is S_4.

3.3.3 Dihedral Symmetry

The dihedral symmetry group includes the dihedral group (D_n), the prismatic group (D_{nh}) and the antiprismatic group (D_{nd}). The symmetry elements for the D_n group are E, C_n, and nC_2 (C_n) and the symmetry operation are [E, C_n^k(k=1, … ,n-1), nC_2] while the order is 2n. Example of molecule in this group is $[Co(en)_3]^{3+}$ which is D_3.

The D_{nh} group has symmetry elements, E, C_n, ₕ,and nC_2 (C_n) and the corresponding symmetry operation are {E, C_n^k(k=1, … ,n-1), ?ₕ, S_n^m(m=1, … ,n-1), nC_2, n ᵥ} while the order of the group is 4n. Benzene is an example of molecule in this group and has D_{6h} point group.

The symmetry elements for the anti-prismatic point group (D_{nd}) are E, C_n, d, and nC_2 (C_n) and the corresponding symmetry operation are {E, C_n^k(k=1, … ,n-1), S_{2n}^m(m=1, … ,2n-1), nC_2, n d. The order of the group is 4n. C_2H_6 is a D_{3d} and is an example of molecule in this group.

3. 3.4 Polyhedral Symmetry:

This class includes T, T_h, T_d, O, O_h, I and I_h, which have more than two high-order axes. They can further be classified into cubic (which include the T, T_h, T_d, O and O_h groups) and icosahedral (which include the I and I_h groups) point groups

The cubic groups do not have a C_5 proper rotation axis and consist of T, T_h, T_d, O and O_h groups The symmetry elements for the T group are E, $4C_3$, and $3C_2$ and symmetry operations are {E, $4C_3$, $4C_3^2$, $3C_2$} while the order of the group is 12. For T_h group, symmetry elements are E, $3C_2$, $4C_3$, i, $4S_6$ and 3 ₕ and symmetry operations are {E, $4C_3$, $4C_3^2$, $3C_2$, i, $4S_6$, $4S_6^5$, 3 ₕ. The order of T_h group is 24. For T_d group, symmetry elements are E, $3C_2$, $4C_3$, $3S_4$ and 6 d and the symmetry operations are {E, $8C_3$, $3C_2$, $6S_4$, 6 d. The order of T_d group is 24 and CCl_4 is an example of T_d molecule. Symmetry elements for the O group are E, $3C_4$, $4C_3$, and $6C_2$ and the corresponding symmetry operations are {E, $8C_3$, $3C_2$, $6C_4$, $6C_2$} while the order of O group is 24.

For O_h group, symmetry elements are E, $3S_4$, $3C_4$, $6C_2$, $4S_6$, $4C_3$, 3 ₕ, 6 d, and i. The symmetry operations are {E, $8C_3$, $6C_2$, $6C_4$, $3C_2$, i, $6S_4$, $8S_6$, 3 ₕ, 6 d}The order of O_h group is 48.For example, the point group of SF_6 is O_h.

The icosahedral groups, which consist of the I and I_h groups have C_5 proper rotation axis and the include the I and I_h group. The symmetry elements for the I group are E, $6C_5$, $10C_3$, and $15C_2$ while its symmetry operations are {E, $15C_5$, $12C_5^2$, $20C_3$, $15C_2$}. The order of I group is 60. For I_h group, symmetry elements are E, $6S_{10}$, $10S_6$, $6C_5$, $10C_3$, $15C_2$ and 15 and symmetry operations are {E, $15C_5$, $12C_5^2$, $20C_3$, $15C_2$, i, $12S_{10}$, $12S_{10}^3$, $20S_6$, 15 . The order of I_h group is 120. For example, the point group of C_{60} is I_h. It can be shown that for a group containing a C_5 operation (icosahedral group), the under listed functions are correct.

$$y^+ = \frac{1}{2}\left(1 + 5^{\frac{1}{2}}\right) = 1.61803L = -2cos144°$$

$$\eta^- = \frac{1}{2}\left(1 - 5^{\frac{1}{2}}\right) = -1.61803L = -2cos72°$$

$$y^+\eta^+ = 1 + \eta^+ and\, \eta^-\eta^- = 1 + \eta^-.\, Therefore, \quad \eta^+\eta^- = -1$$
$$2cos144° + 2cos72°,\, therefore, \quad \eta^+ + \eta^- = 1$$

The Linear group

This class includes C_v and D_h, which are the symmetry of linear molecules. The symmetry elements for the C_v are E, C and $_v$. CO, HCN, NO, HCl are examples of molecules in this class. For the D_h group, symmetry elements are E, C $_v$, $_h$, i, and C_2. Example of molecules in this point groups are CO_2, O_2 and N_2.

3.4   Properties of Symmetry Group

Generally, the basic properties of a group are

i.   **Associativity**: All the elements in the group must satisfy the law of associativity, which can be expressed as (AB)C=A(BC).
ii.   **Closure**: If two elements A and B are in the group G, then the multiplicity of these two elements, C, is also in this group.
iii.   **Identity**: The group must contain such an element E that ER=RE=R
     In group theory, it refers to the operation identity E. Because any molecule or substance must at least have the symmetry element E.
iv.   **Inverses**: If A is an element in group G, there must be another element A^{-1} in group G that satisfies $AA^{-1} = A^{-1}A=E$.

3.5   Application of Symmetry and Group Theory

Symmetry can be used to predict numerous chemical properties of molecules such as dipole moment and allowed spectroscopic transition such as prediction of intra red or Raman active vibrations in a molecule;

Group theory, which classifies molecules to unique symmetry groups offers outfits for studying molecular orbitals with references to methods such as Huckel method, ligand field theory and the Woodward Hoffmann rules. The structure and behavior of molecules and crystals depend on their different symmetries, group theory is an essential theoretical tool to aid the prediction of some characteristic properties of molecules. Solutions obtained from quantum mechanics for some chemical problems ends with complicated mathematics but those from group theory are simplified and easy to follow.

Crystal symmetry is useful in describing crystallography symmetry in bulk materials. Apart from computational chemistry calculations, there are practical techniques that can be used to assess molecular symmetry. X-ray crystallography is one of such methods

Self Assessment Exercises

1.   What are the irreducible and reducible symmetry elements for the C_{4v} point group
2.   How many line of symmetry has cyclopropane. Show this using an equilateral triangle
3.   Draw the following shapes and identify the number of lines of symmetry for each of them: rhombus, square and a scalene triangle.
4.   List the symmetry elements for water molecule
5.   What is the symmetry elements for tetrachlropalladate, $[PdCl_4]^{2-}$

Answer to Self Assessment Exercise

1.   The symmetry elements for C_{4v} point group are $E, C_4, C_4^2, C_4^3, \sigma_v', \sigma_v'', \sigma_d'$ and σ_d''. This consist of eight (8) reducible elements, which can be reduced to five (5) irreducible elements as follows, $C_{4V} \equiv E, 2C_4, C_2, 2\sigma_v$ and $2\sigma_d$

2.   Cyclopropane has three lines of symmetry. This can be represented as,
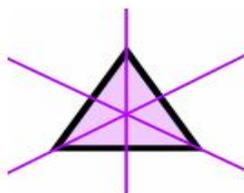
3. The number of line of symmetry are as follows,
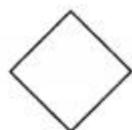
A rhombus — Number of lines of symmetry = 2

A square — Number of lines of symmetry = 4

A scalene triangle — Number of lines of symmetry = 0

4.   Water molecule belongs to C_{2v} point group. The symmetry elements are E, σ_V, σ_V' and C_2

5.   The symmetry elements for tetrachlropalladate are E, i, $C4$, $4C_2$, S_4, $_h$, 2 $_v$ and 2 $_d$

4.0   CONCLUSION

A symmetry operation is an act upon whose execution the resulting molecular appearance is indistinguishable from the one before that operation was executed. The presence of symmetry in a molecule greatly reduces the effort in predicting the nature of some molecular properties. Although visual inspection can reveal the presence (or lack) of symmetry in a given molecule, a systematic approach to characterize that symmetry is desirable. The theory of point groups provides one such approach.

5.0   SUMMARY

A point group is a collection of symmetry operations that satisfy, as a group, certain characteristics and leave a point in a molecule unaffected. Based on the type and number of symmetry operations present, a molecule can be classified to belong to a certain point group. Regardless of the number or type of symmetry elements (or operations) a given molecule possesses, every molecule has an identity element (or an operation), E. This symmetry operation is no more than doing nothing. That is, every atom in a given molecule transforms into itself upon identity operation

6.0   TUTOR MARAKED ASSIGNMENT

(1)   What are the applications of symmetry in crystallography and in organic chemistry   (4 minutes)
(2)   Draw the structure of cyclobutene and indicates all the symmetry ele,emts when the molecule is progressively rotated at 90 ° until identity element is obtained.   6 minutes)

7.0   REFERENCES/FURTHER READINGS

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MODULE 3

UNIT 2   HEAT CAPACITY OF SOLID AND CRYSTALS

1.0   Introduction
2.0   Intended Learning outcome
3.0   Main Content
      3.1   Theoretical Consideration of Heat Capacity
4.0   (i)   Self Assessment Exercise and Answers
      (ii)   Class Activity
5.0   Conclusion
6.0   Summary
7.0   References/Further Readings

1.0   INTRODUCTION

In 1819 by French physicists Pierre Louis Dulong and Alexix Therese Petit, proposed a thermodynamic law and states the classical expression for the molar specific heat capacity of certain chemical elements. Experimentally the two scientists had found that the heat capacity per weight (the mass-specific heat capacity) for a number of elements was close to a constant value, *after* it had been multiplied by a number representing the presumed relative atomic weight of the element. These atomic weights had shortly before been suggested by John Dalton and modified by Jacob Berzelius.

In modern terms, Dulong and Petit found that the heat capacity of a mole of many solid elements is about 3R, where R is the modern constant called the universal gas constant. Dulong and Petit were unaware of the relationship with R, since this constant had not yet been defined from the later kinetic theory of gases. The value of 3R is about 25 J/K, and Dulong and Petit essentially found that this was the heat capacity of certain solid elements per mole of atoms they contained.

The modern theory of the heat capacity of solids states that it is due to lattice vibration the solid and was first derived in crude form from this assumption by Albert Einstein in 1907. The Einstein soldi model thus gave for the first time a reason why the Dulong–Petit law should be stated in terms of the classical heat capacities for gases.

3.0   MAIN CONTENT

3.1   Theoretical Consideration of Heat Capacity

As sated before, heat capacity is defined as the amount of heat absorbed per unit change in temperature. Thermodynamics reveals that the heat absorbed at constant volume is called the internal energy change. Therefore, the heat capacity at constant volume can be written as,

$$C_V = \frac{\partial U}{\partial T}$$

If the substances is a gas, the physical state of the compound and the conditions heat is transferred (i.e constant volume or constant pressure). However, for solid, these factors are relatively negligible, hence we can state that the heat capacity of solid is

$$C = \frac{\partial U}{\partial T} \qquad\qquad\qquad 6.1$$

Simple harmonic oscillator model can be applied to described heat capacity of a solid. If a solid is considered to be a three-dimensional lattice arrangement of atoms held (near equilibrium) together by strong forces of interaction. The force on the atom is said to be simple harmonic if there is a deviation from the equilibrium position. Consequently, when there is no displacement, the force is zero indicating that when the deviation is small, the force is proportional to the deviation. Any solid that obeys this model can be said to compose of harmonic oscillators. For example, in a cubic crystal, the atoms is free to oscillate in three dimensions.

In a one dimension, the average energy of a harmonic oscillator is kT (k = Boltzmann's constant). Therefore, for three dimensions, the average energy will be 3kT. For N number of atoms in the lattice, the internal energy, U = N(3kT). If this is divided by Avogadro's number (A = 6.025 × 10^{23}), we have,

$$U = \left(\frac{N}{A}\right)\left(\frac{3AkT}{1}\right) = 3nAkT \qquad\qquad 6.2$$

where n is the number of moles ($n = \frac{N}{A}$), U is the internal energy, k is the Boltzmann constant and T is the temperature is Kelvin unit. Therefore, the heat capacity per unit mole can be defined as,

$$U_m = \frac{U}{n} = 3AkT = 3RT \qquad\qquad 6.3$$

Since $C = \frac{\partial U}{\partial T}$, then,

$$\frac{\partial U_m}{\partial T} = \frac{\partial (3RT)}{\partial T} = 3R \qquad\qquad 6.4$$

Therefore, it can be stated that the heat capacity of a solid at constant pressure (C_p) is equal to 3R (which is approximately equal to 6 calories per degree Kelvin). This value is called Dulong and Petit value. At room temperature (300 K), most solid obey Dulong and Petit law. However, at low temperature, the most solid witness deviation from this law. For example, a plot of heat capacity of metallic silver as a function of temperature is shown in Fig. 6.1
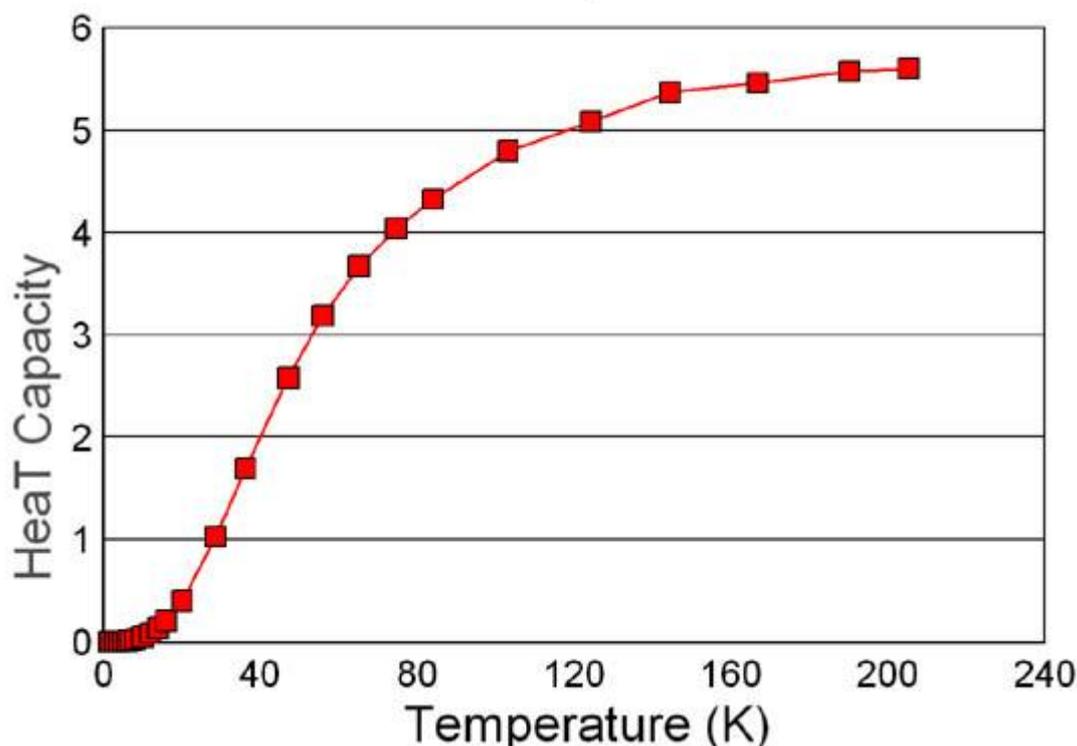
Fig. 6.1: Variation of heat capacity of silver metal with temperature

The shape of the curve for T near zero reveals that the heat capacity is proportional to a power of T, that is T^2 or T^3. Dulong and Petit found that the heat capacity of amole of many solid elements is about $3R$, where R is the modern constant called the universal gas constant. An equivalent statement of the Dulong–Petit law in modern terms is that, regardless of the nature of the substance, the specific heat capacity of a solid element (measured in joule per kelvin per kilogram) is equal to $3R/M$, where R is the gas constant (measured in joule per kelvin per mole) and M is the molar mass (measured in kilogram per mole). Thus, the heat capacity per mole of many elements is $3R$.Planck's law of distribution of energy for an ensemble (collection) of harmonic oscillators gives the average energy E as,

$$E = \frac{\hbar\omega}{\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]} \qquad\qquad 6.5$$

where $\hbar = \frac{h}{2\pi}$ and is called reduced Planck constant, ω is the characteristic frequency (circular) of oscillation. ω depends on the nature of the solid. Temperatures that makes $kT \gg \hbar\omega$, approximate the energy value (according to equation 6.5) to kT. Generally, from definition of internal energy, that is the total energy a molecule possesses, that is, $U = N\sum E$, we have

$$U = N\sum E = \frac{3N\hbar\omega}{\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]} \qquad\qquad 6.6$$

$$U_M = U/n = \frac{AN}{N}\sum E = \frac{3A\hbar\omega}{\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]} \qquad\qquad 6.7$$

$$C_p = \frac{\partial U_m}{\partial T} = \frac{-3A\hbar\omega}{\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]^2\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]\left(\frac{-\hbar\omega}{kT^2}\right)} \qquad\qquad 6.8$$

Equation 6.8 can be re-arranged into the form shown in equation 6.9

$$C_p = \frac{3R\left(\frac{\hbar\omega}{kT}\right)^2 exp\left(\frac{\hbar\omega}{kT}\right)}{\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]^2} \qquad\qquad 6.9$$

Division of the numerator and denominator of equation 6.8 by $\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]^2$, leads to equation 6.10

$$C_p = \frac{3R\left(\frac{\hbar\omega}{kT}\right)^2 exp\left(\frac{-\hbar\omega}{kT}\right)}{\left[1-\exp\left(-\frac{\hbar\omega}{kT}\right)\right]^2} \qquad\qquad 6.10$$

Attempt to obtain the limit of this expression as T 0 will produces ambiguous result of / . However, the application of l'Hospital's Rule two times will finally produces the result that the limit of C_p is zero as T 0.

As observed from Fig. 6.1, the empirical heat capacity curve for silver seems to be proportional to T^2 or T^3 for small values of T. The graph of the quantum mechanical heat capacity function derived above indicates that for values of T near zero the heat capacity function is zero and flat as shown in Fig. 6.2.
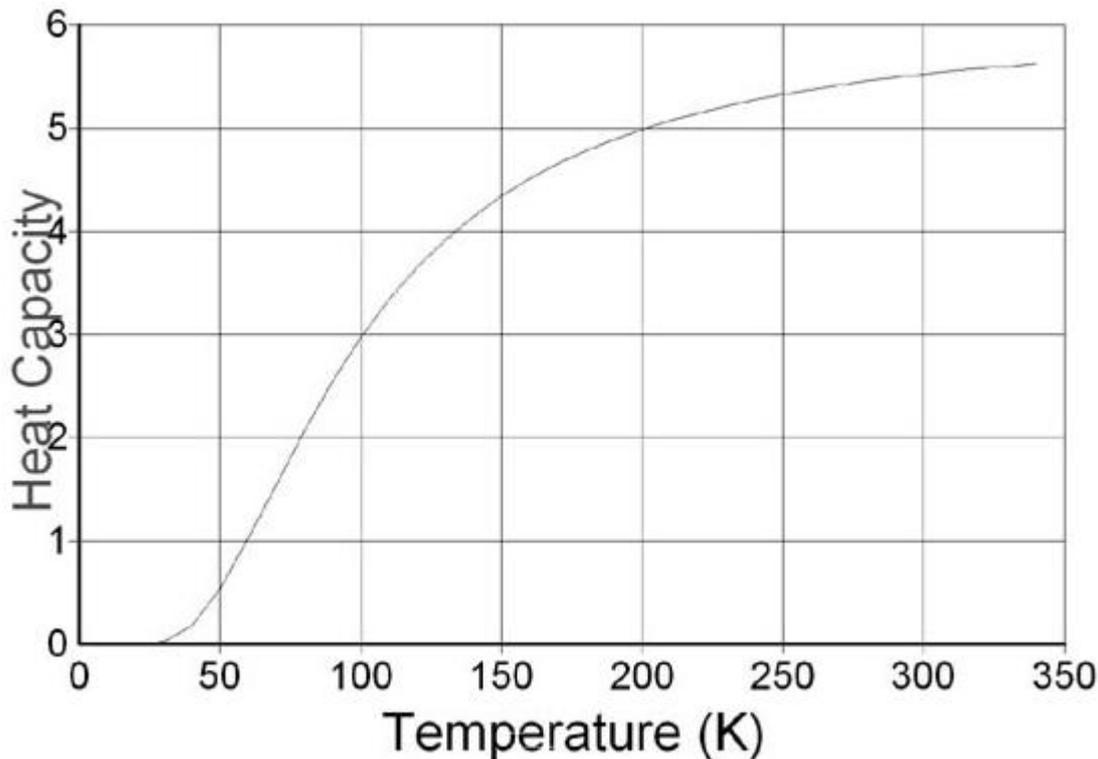
Fig. 6.2: Variation of heat capacity of metallic silver with temperature ranging from 0 to 350 K

The function, $\frac{\hbar\omega}{k}$ has the same dimension as temperature and can be denoted as, θ. θ is called the Einstein temperature. Consequently, the heat capacity function can be written by replacing $\frac{\hbar\omega}{k}$ in equation 6.10 with θ, which gives

$$C_p = \frac{3R\left(\frac{\theta}{T}\right)^2 exp\left(\frac{-\theta}{k}\right)}{\left[1-exp\left(-\frac{\theta}{T}\right)\right]^2} \qquad\qquad 6.11$$

Also, by replacing θ/T with z, we have,

$$C_p = \frac{3Rz^2 exp(-z)}{[1-exp(-z)]^2} \qquad\qquad 6.12$$

$$lnC_p = \ln(3R) + 2\ln(z) - 2\ln[(1-exp(-z)] \qquad 6.13$$

The implication of equation 6.13 is that ln (C_p) –   as z   + ; i.e., C_p 0 as T   0.

(i)   Self Assessment Exercises

1.   Given t Given that $C_p = \frac{3R\left(\frac{\hbar\omega}{kT}\right)^2 exp\left(\frac{-\hbar\omega}{kT}\right)}{\left[1-exp\left(-\frac{\hbar\omega}{kT}\right)\right]^2}$, Use l'Hospital's Rule to show that C_p 0 as T   0

2.   How much energy (in J) is lost when a sample of iron with a mass of 25.7 g cools   from   75 to 22 °C (Specific heat of iron, C= 0.450J/g/°C.

3.   What is the specific heat of lead in J/g//°C, if it takes 97.6 J97.6 J
       to raise the temperature   of a 75.2 g of block by 10.0°C?
4.   What is the heat capacity of 83 g of mercury? The specific heat of
       mercury = 0.14 J/g/°C
5.   In the lab, an experimenter mixes 9.0 g of water (initially at 23.4
       °C) with 80 g of a solid   metal (initially at 350 °C). At thermal
       equilibrium, he measures a final temp of 55.4 °C .   What
       must the specific heat of the metal be?

Answers to Self Assessment Exercise

1.   The term, $\left[1 - \exp\left(-\frac{\hbar\omega}{kT}\right)\right]^2$ can be ignore because it approaches
the limit of 1 as T→0, thus equation 6.10 becomes

$$C_p = 3R\left(\frac{\hbar\omega}{kT}\right)^2 \exp\left(\frac{-\hbar\omega}{kT}\right)$$

Since the term, $\frac{\hbar\omega}{k}$ has the same dimension with temperature, it can be
replaced with θ and the above equation becomes,

$$C_p = 3R\left(\frac{\theta}{T}\right)^2 \exp\left(\frac{-\theta}{T}\right)$$

When T goes to zero the above expression goes to --/ . By l'Hospital's
Rule we should consider the limit of the derivatives of the numerator
and denominator. Thus

$$\frac{3R(2(\theta^2))\left(\frac{1}{T^3}\right)}{\left[\exp\left(\frac{\theta}{T}\right)\left(-\frac{\theta}{T^2}\right)\right]} = 6R\theta\left(\frac{1}{T}\right)\exp\left(\frac{\theta}{T}\right)$$

The above expression gives to ∞/∞, at the limit the temperature tends to
zero. However, the l'Hospital's rule must be applied again, which gives

$$6R\theta\left(\frac{1}{T^2}\right)\exp\left(\frac{\theta}{T}\right)\left(\frac{\theta}{T^2}\right) = \frac{6R}{\exp\left(\frac{\theta}{T}\right)}$$

From the above, C_p 0 as T   0.

2.   **Given**

Mass of iron m =25.7 gm = 25.7 g
Change in temperature   T=22.0 –75.0 =–53 °C
Specific Heat of iron C= 0.450J/g/°C
The heat loss is given as, Q=mC T = 25.7 g(0.450J/g/°C)(-53°C) = -
612.945 J

Therefore, the energy loss is 612.945 J

3.   Given:
Heat Energy Q=97.6 J
Change in Temperature   T=10 °C
Mass of the lead m = 75.2 gm =75.2 g
But Q = mCΔT, indicating that C is given as,

$$C = \frac{Q}{m\Delta T} = \frac{97.6J}{(75.2g)(10\ °C)} = 0.1298\frac{J}{g}/°C$$

Therefore, the specific heat capacity of lead is 0.130 J/g/°C
4. Heat capacity, C is related to specific heat capacity as follows,
$$C = mass \times specific\ heat\ capacity = 83\ g(0.14\ J/(g°C)$$
$$\approx 12\ J/°C$$
5.   The first step involves calculating the energy gained by the water, thus,

$$E = 9 \times 4.186\ (55.4 - 23.4) = 1205.6\ J$$
$$\Delta T = (350 - 55.4)°C = 294.6\ °C$$

Consequently, 1205.6 J of energy was gained by the metal. Hence, $1205.6\ J = mC\Delta T$ and

$$C = \frac{1205.6\ J}{\Delta Tm} = \frac{1205.6\ J}{(80g)(294.6\ °C)} = 0.0512\ J/K/g$$

(ii)   Class Activity
(1)   A 0.500 kg aluminium pan on a stove is used to heat 0.250 liters of water from 20.0 °C to   80.0C (a) How much heat is required? What percentage of the heat is used to raise the   temperature of (b) the pan and (c) the water?   (10 minutes)

4.0   CONCLUSION

Crystal solids behaves differently from ordinary solid indicating that molecular vibrations in crystals also differs. Specific heat is an intrinsic property of a substance that is the measure of heat energy required to raise a unit mass of a substance by one-unit degree. Specific heat can be used to solve for the heat absorbed or heat loss by the substance depending on the change in temperature..

5.0   SUMMARY

This study section analysed theoretical framework for the prediction of heat capacity of solid crystal. Unlike gases and liquid, conditions of operation (that is constant pressure or constant volume) is negligible in solids. There are two basic models that explain the heat capacity of solid. These are Dulong and Petit law and Einstein law. Both laws reveals that as the temperature tends to zero, the heat capacity also tend

to zero and that heat capacity has some exponential relationship with temperature.

6.0   TUTOR MARKED ASSIGNMENT

7.0   REFERENCES/FURTHER READINGS

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