NATIONAL OPENUNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 313

COURSE TITLE: Atomic and Molecular Structure and Symmetry

Course Code	CHM 313
Course Title	Atomic and Molecular Structure and Symmetry
Course Developer/Writer	Dr N. A. A. Babarinde Department of Chemical Sciences, Faculty of Science, Olabisi Onabanjo University, Ago-Iwoye, Ogun State, Nigeria.
Course Editor	
Programme Leader	
Course Coordinator	

CONTENTS PAGE

Introduction ………………………………………………………………….. 1

What you will Learn in this Course ……………………………………….……… 1

Course Aims ……………………………………………………………….…… 2

Course objectives ………………………………………………………………… 2

Working through this Course …………………………………………………. 4

The Course Material …………………………………………………………….. 4

Study Units …………………………………………………………………….... 5

Presentation Schedule ……………………………………………………. 8

Assessment ………………………………………………………………. 8

Tutor- Marked Assignment …………………………………………………. 8

Final Examination and Grading …..………………………………………….. 9

Course Marking Scheme …………………………………………………….. 9

Facilitators/Tutors and Tutorials …………………………………………….. 9

Summary ………………………….………………………………………….. 10

Introduction

Atomic and molecular structure and symmetry is a first harmattan semester course. It is a three credit degree course available to all students offering Bachelor of Science (B.Sc.) Chemistry. It majorly concerns the theoretical studies of the atomic and molecular structures. The interaction of the molecules with electromagnetic radiation is what is called spectroscopy. **Spectroscopy** is an analytical technique concerned with the measurement of the interaction (usually the absorption or the emission) of radiant energy with matter, with the instruments necessary to make such measurements, and with the interpretation of the interaction both at the fundamental level and for practical analysis. A display of such a data obtained from the interaction (usually the absorption or the emission) of radiant energy with matter is called a spectrum. It is a plot of the intensity of emitted or transmitted radiant energy (or some function of the intensity) versus the energy of that light. Spectra due to the emission of radiant energy are produced as energy is emitted from matter, after some form of excitation, then collimated by passage through a slit, then separated into components of different energy by transmission through a prism (refraction) or by reflection from a ruled grating or a crystalline solid (diffraction), and finally detected. Spectra due to the absorption of radiant energy are produced when radiant energy from a stable source, collimated and separated into its components in a monochromator, passed through the sample whose absorption spectrum is to be measured, and is detected. Instruments which produce spectra are variously called spectroscopes, spectrometers, spectrographs, and spectrophotometers.

> Interpretation of spectra provides fundamental information on atomic and molecular energy levels, the distribution of species within those levels, the nature of processes involving change from one level to another, molecular geometries, chemical bonding, and interaction of molecules in solution. At the practical level, comparisons of spectra provide a basis for the determination of qualitative chemical composition and chemical structure, and for quantitative chemical analysis.

What you will learn in this course

The course consists of units and a course guide. This course guide tells you briefly what the course is all about, what course materials you will be using and how you can work with these materials. In addition, it advocates some general guidelines for the amount of time you are likely to spend on each unit of the course in order to complete it successfully.

It gives you guidance in respect of your Tutor Marked Assignment which will be made available in the assignment file. There will be regular tutorial classes that are related to the course. It is advisable for you to attend these tutorial sessions. The course will prepare you for the challenges you will meet in the field of Atomic and molecular structure and Symmetry.

Course Aims

The aim of the course is not complex. The course aims to provide you with an understanding of Atomic and molecular structure and Symmetry; it also aims to provide you with solutions to problems in Atomic and molecular structure and Symmetry.

Course Objectives

To achieve the aims set out, the course has a set of objectives. Each unit has specific objectives which are included at the beginning of the unit. You should read these objectives before you study the unit. You may wish to refer to them during your study to check on your progress. You should always look at the unit objectives after completion of each unit. By doing so, you would have followed the instructions in the unit.

Below are the comprehensive objectives of the course as a whole. By meeting these objectives, you should have achieved the aims of the course as a whole. In addition to the aims above, this course sets to achieve some objectives. Thus, after going through the course, you should be able to:

- Define and distinguish between shells, subshells, and orbitals;
- Explain the relationships between the quantum numbers;
- List a set of subshells in order of increasing energy;
- Write electron configurations for atoms in either the subshell or orbital box notations;
- Write electron configurations of ions;
- Define Pauli Exclusion Principle and the Hund’s rule;

- Define molecular orbital;
- Explain how molecular orbital are formed;
- Give the consequence from molecular orbital theory;
- Use bond order to determine the possibility of bond formation in molecules.
- Define atomic spectra;
- Explain the origin of atomic spectra;
- Calculate the wavelength in the atomic spectra of hydrogen;
- Explain the five series for atomic spectra of hydrogen;
- Define heat capacity;
- Derive the heat Capacity function for low temperatures;
- Define Hybridization of atomic orbitals;
- How a chemical bond is formed;
- Define modern valence theory;
- Write wave function as a linear combination of two functions;
- Define what molecular orbital theory is;
- Define properties of molecular orbital;
- Illustrate pictorially molecular orbitals for several organic and inorganic molecules;
- Define what resonance is;
- Explain what resonance energy is;
- Explain what vector analogy of resonance is;
- Explain the difference between bonding and antibonding orbitals;
- Draw Molecular orbital energy diagrams for diatomic molecules;
- Show the relationships between bond order and each of bond dissociation energy, bond length and force constant;
- Define quantum chemistry;
- Explain the history of quantum chemistry;
- Explain the Usefulness of quantum mechanics;
- Give the postulates of quantum mechanics;
- Define an operator;

- Explain the usefulness of wavefunction;
- Uncertainty principle;
- Define particle in a box;
- Define the terms in the time-independent Schrodinger wave equation;
- Write the equation for probability of find a particle within the box;
- Calculate the wave number for transition in a conjugated system;
- Write equation for the 3D Schrodinger wave equation;
- Draw the diagram for the quantized energy levels of a particle in a 3D;
- Calculate the energy difference when there is transition between two energy levels;
- Write the Schrodinger wave equation for the hydrogen molecule ion;
- Write the Schrodinger wave equation for the hydrogen molecule;
- Draw the potential energy curve for a diatomic molecule;
- Define what spectroscopy is;
- Explain the theory of rotational spectroscopy;
- Define what vibrational spectroscopy is;
- Explain the theory of vibration spectroscopy;
- Explain vibrational coordinates;
- Calculate the correct vibration frequencies using Newtonian mechanics;
- Relate the intensity of a spectral line to the population of the initial state;
- Explain isotope effect;
- Explain the theory of Electronic spectroscopy;
- Explain Franck-Condon Principle;
- Use Franck-Condon Principle to account for the vibrational structure of electronic transitions;
- Define symmetry elements and symmetry operations;
- Detect the presence of an axis of symmetry, plane of symmetry, centre of symmetry, and an axis of improper rotation in a body;
- Classify molecules according to their point group symmetry and
- Use the knowledge of symmetry of a molecule deduce whether it can be polar or optically active.

Working through this course

To complete this course, you are required to read each study unit, read the text books and other materials which may be provided by the National Open University of Nigeria. Each unit contains self assessment exercises and at certain points in the course you would be required to submit assignments for assessments purposes. At the end of the course there is a final examination. The course should take you about a total of **17 weeks** to complete. Below, you will find listed all the components of the course, what you have to do and how you should allocate your time to each unit in order to complete the course on time and successfully. The course entails that you spend a lot of time to read. I would advice that you have the opportunity of comparing your knowledge with that of other people.

The Course Materials

The main components of the course are;

1. The course Guide
2. Study Units
3. References/ Further Readings
4. Assignments
5. Presentation Schedule

Study Unit

The study units in this course are as follows:

Module 1 Atomic and molecular structures

Unit 1 Electron configuration

Unit 2 Pauli exclusion principle and the Hund’s rule

Unit 3 Molecular orbitals of molecules

Unit 4 Atomic Spectra

Unit 5 Heat Capacities of solids

Module 2 Theory of Chemical bonding

Unit 1 The Valence Bond Theory

Unit 2 The Molecular orbital Theory

Unit 3 Resonance

Unit 4 Angular momentum

Unit 5 Bonds in Molecules

Module 3 Quantum Mechanics

Unit 1 Introduction to Quantum chemistry

Unit **2** Orbitals, states and wavefunctions

Unit 3 The Particle in a one dimensional (1D) box problem

Unit 4 Particle in a Three-Dimensional (3D) Box

Unit 5 Application of Schrodinger wave equation to bonding in molecules

Module 4 Theory of molecular spectroscopy

Unit 1 Rotational spectroscopy

Unit 2 Vibrational spectroscopy

Unit 3 Vibrational rotational spectroscopy

Unit 4 Electronic spectroscopy

Unit 5 Introduction to symmetry

Unit 6 Application of symmetry

In Module 1, the first and second units focus on the structure of the atoms with regard to the arrangement of electrons in their orbitals. The third unit focuses on the formation of molecular orbitals from atomic orbitals. The fourth unit is concerned about atomic spectra, which gives insight into the possibility of electrons moving between levels as a result of absorption or release of energy. In unit 5, the heat capacities of solids are treated from theoretical angle.

In Module 2, the first two units focus on valence bond theory and molecular orbital theory, as basic theories developed to use the methods of quantum mechanics to explain chemical bonding. The valence bond theory focuses on how the atomic orbitals of the dissociated atoms combine on molecular formation to give individual chemical bonds. In contrast, molecular orbital theory has orbitals that cover the whole molecule. Molecular orbital theory (*MO theory*) is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. In this theory, each molecule has a set of molecular orbitals, in which it is assumed that the molecular orbital wave function ψ_f may be written as a simple weighted sum of the n constituent atomic orbitals χ_i.

Unit 3 is concerned about resonance. It is a key component of valence bond theory used to graphically represent and mathematically model certain types of molecular structures when no single, conventional Lewis structure can satisfactorily represent the observed structure or explain its properties. Resonance instead considers such molecules to be an intermediate or average (called a **resonance hybrid**) between several Lewis structures that differ only in the placement of the valence electrons.

Unit 4 focuses on angular momentum which is a property of a physical system that is a constant of motion (is time-independent and well-defined) in two situations: (i) The system experiences a spherical symmetric potential field. (ii) The system moves (in quantum mechanical sense) in isotropic space. In both cases the angular momentum operator commutes with the Hamiltonian of the system. By Heisenberg's uncertainty relation this means that the angular momentum can assume a sharp value simultaneously with the energy (eigenvalue of the Hamiltonian).

In Unit 5 the study is on bonds in molecules. When atoms combine to form a molecule, the number of orbitals in the molecule equals the number of orbitals in the combining atoms. When two very simple atoms, each with one atomic orbital, are combined, two molecular orbitals are formed. One is a *bonding* orbital, lower in energy than the atomic orbitals, and derived from their sum. It is called *sigma*. The other is an *antibonding* orbital, higher in energy than the atomic orbitals, and resulting from their difference.

In Module 3, the first unit focuses on introduction to quantum chemistry. Quantum chemistry mathematically describes the fundamental behavior of matter at the molecular scale. It is, in principle, possible to describe all chemical systems using this theory. In practice, only the simplest chemical systems may realistically be investigated in purely quantum mechanical terms, and approximations must be made for most practical purposes. In unit 2, the focus is on the wavefunction as a mathematical function describing the wavelike motion of microscopic object. unit 3 is concerned about the motion of a particle in one dimension. It is the simplest system of physical significance for a particle constrained to move in a box of given dimension. The particle can be confined to certain region in space by allowing the potential energy to be infinite in any region outside that of interest. If the potential energy is zero within the defined region (that is the box), we have a simple system that still has physical application: translational motion of molecules. unit 4 is an extension of unit 3 as it focuses on a particle moving in a three dimensional box. In unit 5, the application of the Schrodinger wave equation to determine the feasibility of bonding in molecules is the focus.

In Module 4, the first unit focuses on rotational spectroscopy or microwave spectroscopy which studies the absorption and emission of electromagnetic radiation (typically in the microwave region of the electromagnetic spectrum) by molecules associated with a corresponding change in the rotational quantum number of the molecule. The second unit deals with the absorption or emission of energy due to vibration of bonds in molecules. The third unit is concerned about the absorption or emission of energy due to combination of rotation and vibration of bonds in molecules. In unit four, the focus is energies involved when molecules make transitions by changing their electronic distributions. In unit 5, the identification of symmetry elements and symmetry operations in molecule is the concern. Finally, in unit 6, the determination of symmetry point group and the application of symmetry in predicting properties of molecules are fully examined.

Each unit consists of one or two weeks' work and include an introduction, objectives, reading materials, exercises or activities, conclusion, summary, Tutor marked assignments (TMAs), references and other resources. The unit directs you to work on exercises related to the required reading. In general, these exercises test you on the materials you have just covered or require you to apply it in some way and thereby assist you to evaluate your progress and to reinforce your comprehension of the material. Together with TMAs, these exercises will help you in achieving the stated learning objectives of the individual units of the course as a whole.

Presentation Schedule

Your course materials have important dates for the early and timely completion and submission of your TMAs and attending tutorials. You should remember that you are required to submit all your assignments by the stipulated time and date. You should guard against falling behind in your work.

Assessment

There are three aspects of the assessment of the course. First is the self-assessment exercise, the second consists of the tutor-marked assignments and the third is the written examination/end of course examination.

You are advised to do the exercises. In tackling the assignments, you are expected to apply information, knowledge and techniques you gathered during the course. The assignments must be submitted to your facilitator for formal assessment in accordance with the deadlines stated in the presentation schedule and the assignment file. The work you submit to your tutor for assessment will count for 30 % of your total course work.

At the end of the course, you will need to sit for a final or end of course examination of about three hour duration. This examination will count for 70 % of your total course mark.

Tutor-marked assignment

The TMA is a continuous assessment component of your course. It accounts for 30 % of the total score. You will be given four (4) TMAs to answer. Three of these must be answered before you are allowed to sit for the end of course examination. The TMAs would be given to you by your facilitator and returned after you have done the assignment. Assignment questions for the units in this course are contained in the assignment file. You will be able to complete your assignment from the information and material contained in your reading, references and study units. However, it is desirable in all degree level of education to demonstrate that you have read and researched more into your references, which will give you a wider view point and may provide you with a deeper understanding of the subject.

Make sure that each assignment reaches your facilitator on or before the deadline given in the presentation schedule and assignment file. If for any reason you cannot complete your work on time, contact your facilitator before the assignment is due to discuss the possibility of an extension. Extension will not be granted after the due date unless there are exceptional circumstances.

Final Examination and Grading

The end of course examination for atomic and molecular structure and symmetry will be for about 3 hours and it has a value of 70 % of the total course work. The examination will consist of questions, which will reflect the type of self-testing, practice exercise and tutor-marked assignment problems you have previously encountered. All areas of the course will be assessed. Use the time between finishing the last unit and sitting for the examination to revise the whole course. You might find it useful to review your self-test, TMAs and comments on them before the examination. The end of course examination covers information from all parts of the course.

Course Marking Scheme

Assignment	Marks
Assignments 1-4	Four assignments, best three marks of the four count at 10 % each to give 30 % of course marks
End of course examination	70 % of overall course marks
Total	100 % of course materials

Facilitators/ Tutors and Tutorials

There are 16 hours of tutorial provided in support of this course. You will be notified of the dates, times, and locations of these tutorials as well as the name and phone number of your facilitator, as soon as you are allocated a tutorial group.

Your facilitator will mark and comment on your assignments, keep a close watch on your progress and any difficulties you might face and provide assistance to you during the course. You are expected to mail your TMA to your facilitator before the schedule date (at least two working days are required). They will be marked by your tutor and returned to you as soon as possible. Do not delay to contact your facilitator by telephone or e-mail if you need assistance.

The following might be circumstances in which you would find assistance necessary, hence you would have to contact your facilitator if:

- You do not understand any part of the study or the assigned readings.
- You have difficulty with the self-tests.
- You have a question or problem with an assignment or with the grading of an assignment.

You should endeavour to attend the tutorials. This is the only chance to have face to face contact with your course facilitator and to ask questions which are answered instantly. You can raise any problem encountered in the course of you study.

To gain much benefit from course tutorials prepare a question list before attending them. You will learn a lot from participating actively in discussions.

Summary

Atomic and molecular structure and symmetry is a course that intends to provide concept of the discipline and is concerned with theoretically explaining the structure of atoms and molecules as well as the transitions they undergo when the interact with electromagnetic radiations. Upon completing this course, you will be equipped with the theoretical basis of the structure of atoms and molecules. In addition, you will be able to answer the following questions:

- Define modern valence theory;
- Write wave function as a linear combination of two functions;
- Define what molecular orbital is;
- Define what molecular orbital theory is;
- Define properties of molecular orbital;
- Define bonding molecular orbital;
- Define antibonding molecular orbital;
- Draw the diagram for the quantized energy levels of a particle in a 3D;
- Calculate the energy difference when there is transition between two energy levels;
- Define what resonance is;
- Define what spectroscopy is;
- Explain the theory of rotational spectroscopy;
- Draw energy diagram for rotational spectroscopy;
- Use rotational spectroscopy to determine the structures of small molecules;
- Detect the presence of an axis of symmetry, plane of symmetry, centre symmetry, and an axis of improper rotation in a body and
- Explain the theory of vibration spectroscopy.

Of course, the list of questions that you can answer is not limited to the above list. To gain the most from this course you should endeavour to apply the principles you have learnt to your understanding of atomic and molecular structure and symmetry.

I wish you success in the course and I hope that you will find it both interesting and useful.

Course Code	CHM 313
Course Title	Atomic and Molecular Structure and Symmetry
Course Developer/Writer	Dr N. A. A. Babarinde Department of Chemical Sciences, Faculty of Science, Olabisi Onabanjo University, Ago-Iwoye, Ogun State, Nigeria.
Course Editor	
Programme Leader	
Course Coordinator	

NATIONAL OPEN UNIVERSITY OF NIGERIA

Module 1: Atomic and Molecular orbitals

Unit 1: Electron configuration

Contents

1.0 Introduction....21

2.0 Objectives....21

3.0 Definition of configuration....22

  3.1 Electron atomic and molecular orbitals....22

  3.2 Notation....23

  3.3 Energy: GroundS state and Excited state....24

  3.4 History....24

  3.5 Aufbau principle....25

  3.6 The periodic table....27

  3.7 Shortcomings of the Aufbau principle....27

4.0 Conclusion....32

5.0 Summary....33

6.0 Tutor marked assignment (TMA) 33

7.0 Further reading and references 33

1.0 Introduction

Like other elementary particles, the electron is subject to the laws of quantum mechanics, and exhibits both particle-like and wave-like nature. Formally, the quantum state of a particular electron is defined by its wave function, a complex-valued function of space and time. According to the Copenhagen interpretation of quantum mechanics, the position of a particular electron is not well defined until an act of measurement causes it to be detected. The probability that the act of measurement will detect the electron at a particular point in space is proportional to the square of the absolute value of the wavefunction at that point.

2.0 Objectives

By the end of this Unit, you should be able to:

(a) Define and distinguish between shells, subshells, and orbitals.
(b) Explain the relationships between the quantum numbers.
(c) Use quantum numbers to label electrons in atoms.
(d) Describe and compare atomic orbitals given the n and ℓ quantum numbers.
(e) List a set of subshells in order of increasing energy.
(f) Write electron configurations for atoms in either the subshell or orbital box notations.
(g) Write electron configurations of ions.

3.0 Definition of configuration

In chemistry, the term "**electron configuration**" refers to the arrangement of electrons; as they "orbit" around the nuclei of one, or more, atoms. It is the arrangement of electrons of an atom, a molecule, or other physical structure. It concerns the way electrons can be distributed in the orbitals of the given system (atomic or molecular for instance).

3.1 Electron atomic and molecular orbitals

Energy is associated to each electron configuration and, upon certain conditions; electrons are able to move from one orbital to another by emission or absorption of a quantum of energy, in the form of a photon. Knowledge of the electron configuration of different atoms is useful in understanding the structure of the periodic table of elements. The concept is also useful for describing the chemical bonds that hold atoms together. In bulk materials this same idea helps explain the peculiar properties of lasers and semiconductors, shells and subshells. Electron configuration was first conceived of under the Bohr model of the atom, and it is still common to speak of shells and subshells despite the advances in understanding of the quantum-mechanical nature of electrons.

An electron shell is the set of allowed states an electron may occupy which share the same principal quantum number, n (the number before the letter in the orbital label). An electron shell can accommodate $2n^2$ electrons, *i.e.* the first shell can accommodate 2 electrons, the second shell 8 electrons, the third shell 18 electrons, *etc*. The factor of two arises because the allowed states are doubled due to electron spin—each atomic orbital admits up to two otherwise identical electrons with opposite spin, one with a spin +1/2 (usually noted by an up-arrow) and one with a spin -1/2 (with a down-arrow).

A subshell is the set of states defined by a common azimuthal quantum number, *l*, within a shell. The values $l = 0, 1, 2, 3$ correspond to the *s*, *p*, *d*, and *f* labels, respectively. The number of electrons which can be placed in a subshell is given by $2(2l + 1)$. This gives two electrons in an s subshell, six electrons in a p subshell, ten electrons in a d subshell and fourteen electrons in an f subshell.

The numbers of electrons that can occupy each shell and each subshell arise from the equations of quantum mechanics, in particular the Pauli Exclusion Principle, which states that no two electrons in the same atom can have the same values of the four quantum numbers.

3.2 Notation

A standard notation is used to describe the electron configurations of atoms and molecules. For atoms, the notation consists of a string of atomic orbital labels (e.g. 1s, 2p, 3d, 4f) with the number of electrons assigned to each orbital (or set of orbitals sharing the same label) placed as a superscript. For example, hydrogen has one electron in the s-orbital of the first shell, so its configuration is written $1s^1$. Lithium has two electrons in the 1s-subshell and one in the (higher-energy) 2s-subshell, so its configuration is written $1s^2\ 2s^1$ (pronounced "one-s-two, two-s-one"). Phosphorus (atomic number 15), is as follows: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$.

For atoms with many electrons, this notation can become lengthy and so an abbreviated notation is used, noting that the first few subshells are identical to those of one or another of the noble gases. Phosphorus, for instance, differs from neon ($1s^2\ 2s^2\ 2p^6$) only by the presence of a third shell. Thus, the electron configuration of neon is pulled out, and phosphorus is written as follows: [Ne] $3s^2\ 3p^3$. This convention is useful as it is the electrons in the outermost shell which most determine the chemistry of the element.

The order of writing the orbitals is not completely fixed: some sources group all orbitals with the same value of *n* together, while other sources (as here) follow the order given by Madelung's rule. Hence the electron configuration of iron can be written as [Ar] $3d^6\ 4s^2$ (keeping the 3d-electrons with the 3s- and 3p-electrons which are implied by the configuration of argon) or as [Ar] $4s^2$ $3d^6$ (following the Aufbau principle, see below).

The superscript 1 for a singly-occupied orbital is not compulsory. It is quite common to see the letters of the orbital labels (s, p, d, f) written in an italic or slanting typeface, although the International Union of Pure and Applied Chemistry (IUPAC) recommends a normal typeface (as used here). The choice of letters originates from a now-obsolete system of categorizing spectral lines as "sharp", "principal", "diffuse" and "fine", based on their observed fine structure: their modern usage indicates orbitals with an azimuthal quantum number, l, of 0, 1, 2 or 3 respectively. After "f", the sequence continues alphabetically "g", "h", "i"... (l = 4, 5, 6...), although orbitals of these types are rarely required. The electron configurations of molecules are written in a similar way, except that molecular orbital labels are used instead of atomic orbital labels.

3.3 Energy: Ground State and Excited state

The energy associated to an electron is that of its orbital. The energy of a configuration is often approximated as the sum of the energy of each electron, neglecting the electron-electron interactions. The configuration that corresponds to the lowest electronic energy is called the ground-state. Any other configuration is an excited state.

3.4 History

Niels Bohr (1923) was the first to propose that the periodicity in the properties of the elements might be explained by the electronic structure of the atom. His proposals were based on the then current Bohr model of the atom, in which the electron shells were orbits at a fixed distance from the nucleus. Bohr's original configurations would seem strange to a present-day chemist: sulfur was given as 2.4.4.6 instead of $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^4$ (2.8.6).

The following year, E. C. Stoner incorporated Sommerfeld's third quantum number into the description of electron shells, and correctly predicted the shell structure of sulfur to be 2.8.6. However neither Bohr's system nor Stoner's could correctly describe the changes in atomic spectra in a magnetic field (the Zeeman effect).

Bohr was well aware of this shortcoming (and others), and had written to his friend Wolfgang Pauli to ask for his help in saving quantum theory (the system now known as "old quantum theory"). Pauli realized that the Zeeman effect must be due only to the outermost electrons of the atom, and was able to reproduce Stoner's shell structure, but with the correct structure of subshells, by his inclusion of a fourth quantum number and his exclusion principle (1925):

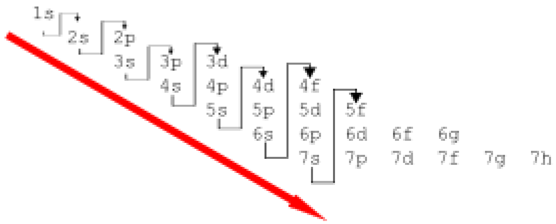
It should be forbidden for more than one electron with the same value of the main quantum number n *to have the same value for the other three quantum numbers* k *[*l*],* l *[*m_l*] and* m *[*m_s*].*

The Schrödinger equation, published in 1926, gave three of the four quantum numbers as a direct consequence of its solution for the hydrogen atom: this solution yields the atomic orbitals which are shown today in textbooks of chemistry (and above). The examination of atomic spectra allowed the electron configurations of atoms to be determined experimentally, and led to an empirical rule (known as Madelung's rule (1936), see below) for the order in which atomic orbitals are filled with electrons.

3.5 Aufbau principle

The Aufbau principle (from the German *Aufbau*, "building up, construction") was an important part of Bohr's original concept of electron configuration. It may be stated as:

> *a maximum of two electrons are put into orbitals in the order of increasing orbital energy: the lowest-energy orbitals are filled before electrons are placed in higher-energy orbitals.*



The approximate order of filling of atomic orbitals, following the arrows.

The principle works very well (for the ground states of the atoms) for the first 18 elements, then increasingly less well for the following 100 elements. The modern form of the Aufbau principle describes an order of orbital energies given by Madelung's rule, first stated by Erwin Madelung in 1936.

1. Orbitals are filled in the order of increasing $n+l$;
2. Where two orbitals have the same value of $n+l$, they are filled in order of increasing n.

This gives the following order for filling the orbitals:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, and 7p

The Aufbau principle can be applied, in a modified form, to the protons and neutrons in the atomic nucleus, as in the shell model of nuclear physics.

3.6 The periodic table

The form of the periodic table is closely related to the electron configuration of the atoms of the elements. For example, all the elements of group 2 have an electron configuration of [E] ns^2 (where [E] is an inert gas configuration), and have notable similarities in their chemical properties. The outermost electron shell is often referred to as the "valence shell" and (to a first approximation) determines the chemical properties. It should be remembered that the similarities in the chemical properties were remarked more than a century before the idea of electron configuration, It is not clear how far Madelung's rule *explains* (rather than simply describes) the periodic table, although some properties (such as the common +2 oxidation state in the first row of the transition metals) would obviously be different with a different order of orbital filling.

3.7 Shortcomings of the Aufbau principle

The Aufbau principle rests on a fundamental postulate that the order of orbital energies is fixed, both for a given element and between different elements: neither of these is true (although they are approximately true enough for the principle to be useful). It considers atomic orbitals as "boxes" of fixed energy into which can be placed two electrons and no more. However the energy of an electron "in" an atomic orbital depends on the energies of all the other electrons of the atom (or ion, or molecule, etc.). There are no "one-electron solutions" for systems of more than one electron, only a set of many-electron solutions which cannot be calculated exactly (although there are mathematical approximations available, such the Hartree–Fock method).

The fact that the Aufbau principle is based on an approximation can be seen from the fact that there is an almost-fixed filling order at all, that, within a given shell, the s-orbital is always filled before the p-orbitals. In a hydrogen-like atom, which only has one electron, the s-orbital and the p-orbitals of the same shell have exactly the same energy, to a very good approximation in the absence of external electromagnetic fields. (However, in a real hydrogen atom, the energy levels are slightly split by the magnetic field of the nucleus, and by the quantum electrodynamics effects of the Lamb shift).

3.8 Ionization of the transition metals

The naive application of the Aufbau principle leads to a well-known paradox (or apparent paradox) in the basic chemistry of the transition metals. Potassium and calcium appear in the periodic table before the transition metals, and have electron configurations [Ar] $4s^1$ and [Ar] $4s^2$ respectively, i.e. the 4s-orbital is filled before the 3d-orbital. This is in line with Madelung's rule, as the 4s-orbital has $n+l = 4$ ($n = 4$, $l = 0$) while the 3d-orbital has $n+l = 5$ ($n = 3$, $l = 2$). However, chromium and copper have electron configurations [Ar] $3d^5$ $4s^1$ and [Ar] $3d^{10}$ $4s^1$ respectively, i.e. one electron has passed from the 4s-orbital to a 3d-orbital to generate a half-filled or filled subshell. In this case, the usual explanation is that "half-filled or completely-filled subshells are particularly stable arrangements of electrons".

The apparent paradox arises when electrons are *removed* from the transition metal atoms to form ions. The first electrons to be ionized come not from the 3d-orbital, as one would expect if it were "higher in energy", but from the 4s-orbital. The same is true when chemical compounds are formed. Chromium hexacarbonyl can be described as a chromium atom (not ion, it is in the oxidation state 0) surrounded by six carbon monoxide ligands: it is diamagnetic, and the electron configuration of the central chromium atom is described as $3d^6$, i.e. the electron which was in the 4s-orbital in the free atom has passed into a 3d-orbital on forming the compound. This interchange of electrons between 4s and 3d is universal among the first series of the transition metals.

The phenomenon is only paradoxical if it is assumed that the energies of atomic orbitals are fixed and unaffected by the presence of electrons in other orbitals. If that were the case, the 3d-orbital would have the same energy as the 3p-orbital, as it does in hydrogen, yet it clearly doesn't. There is no special reason why the Fe^{2+} ion should have the same electron configuration as the chromium atom, given that iron has two more protons in its nucleus than chromium and that the chemistry of the two species is very different. When care is taken to compare "like with like", the paradox disappears.

Table 1.1.1: Electron configuration of elements

Period 5			**Period 6**			**Period 7**		
Element	**Z**	**Electron Configuration**	**Element**	**Z**	**Electron Configuration**	**Element**	**Z**	**Electron Configuration**
Yttrium	39	[Kr] $5s^2$ $4d^1$	Lanthanum	57	[Xe] $6s^2$ $5d^1$	Actinium	89	[Rn] $7s^2$ $6d^1$
			Cerium	58	[Xe] $6s^2$ $4f^1$ $5d^1$	Thorium	90	[Rn] $7s^2$ $6d^2$

		Praseodymium	59	[Xe] $6s^2\ 4f^3$		Protactinium	91	[Rn] $7s^2\ 5f^2\ 6d^1$
		Neodymium	60	[Xe] $6s^2\ 4f^4$		Uranium	92	[Rn] $7s^2\ 5f^3\ 6d^1$
		Promethium	61	[Xe] $6s^2\ 4f^5$		Neptunium	93	[Rn] $7s^2\ 5f^4\ 6d^1$
		Samarium	62	[Xe] $6s^2\ 4f^6$		Plutonium	94	[Rn] $7s^2\ 5f^6$
		Europium	63	[Xe] $6s^2\ 4f^7$		Americium	95	[Rn] $7s^2\ 5f^7$
		Gadolinium	64	[Xe] $6s^2\ 4f^7\ 5d^1$		Curium	96	[Rn] $7s^2\ 5f^7\ 6d^1$
		Terbium	65	[Xe] $6s^2\ 4f^9$		Berkelium	97	[Rn] $7s^2\ 5f^9$

Zirconium	40	[Kr] $5s^2$ $4d^2$		Hafnium	72	[Xe] $6s^2$ $4f^{14}$ $5d^2$		
Niobium	41	[Kr] $5s^1$ $4d^4$		Tantalium	73	[Xe] $6s^2$ $4f^{14}$ $5d^3$		
Molybdenum	42	[Kr] $5s^1$ $4d^5$		Tungsten	74	[Xe] $6s^2$ $4f^{14}$ $5d^4$		
Technetium	43	[Kr] $5s^2$ $4d^5$		Rhenium	75	[Xe] $6s^2$ $4f^{14}$ $5d^5$		
Ruthenium	44	[Kr] $5s^1$ $4d^7$		Osmium	76	[Xe] $6s^2$ $4f^{14}$ $5d^6$		
Rhodium	45	[Kr] $5s^1$ $4d^8$		Iridium	77	[Xe] $6s^2$ $4f^{14}$ $5d^7$		
Palladium	46	[Kr] $4d^{10}$		Platinum	78	[Xe] $6s^1$ $4f^{14}$ $5d^9$		
Silver	47	[Kr] $5s^1$ $4d^{10}$		Gold	79	[Xe] $6s^1$ $4f^{14}$ $5d^{10}$		

Cadmium	48	[Kr] $5s^2$ $4d^{10}$		Mercury	80	[Xe] $6s^2$ $4f^{14}$ $5d^{10}$		
Indium	49	[Kr] $5s^2$ $4d^{10}$ $5p^1$		Thallium	81	[Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^1$		

***Source*: Wikipedia encyclopedia (http//: en.wikipedia.org)**

Activity A

(a) define and distinguish between shells, subshells, and orbitals.
(b) explain the relationships between the quantum numbers.

4.0 Conclusion

Electron configuration is the arrangement of electrons of an atom, a molecule, or other physical structure. It concerns the way electrons can be distributed in the orbitals of the given system (atomic or molecular for instance).

5.0 Summary

In this Unit, we have learnt that:

i. the term "electron configuration" refers to the arrangement of electrons; as they "orbit" around the nuclei of one, or more, atoms.
ii. an energy is associated to each electron configuration and, upon certain conditions; electrons are able to move from one orbital to another by emission or absorption of a quantum of energy, in the form of a photon.
iii. knowledge of the electron configuration of different atoms is useful in understanding the structure of the periodic table of elements.
iv. the molecular orbitals are labeled according to their symmetry, rather than the atomic orbital labels used for atoms and monatomic ions:

6.0 Tutor marked assignment (TMA)

1. use quantum numbers to label electrons in five different atoms.

2. list a set of subshells in order of increasing energy and

3. write electron configurations for atoms in either the subshell for five elements.

7.0 Further reading and references

^ International Union of Pure and Applied Chemistry. "configuration (electronic)". *Compendium of Chemical Terminology* Internet edition.

^ International Union of Pure and Applied Chemistry. " exclusion principle". *Compendium of Chemical Terminology* Internet edition.

^ Bohr, Niels (1923). "Über die Anwendung der Quantumtheorie auf den Atombau. I.". *Z. Phys.* **13**: 117.

^ Stoner, E.C. (1924). "The distribution of electrons among atomic levels". *Phil. Mag. (6th Ser.)* **48**: 719–36.

^ Pauli, Wolfgang (1925). "Über den Einfluss der Geschwindigkeitsabhändigkeit der elektronmasse auf den Zeemaneffekt". *Z. Phys.* **31**: 373. English translation from Scerri, Eric R. (1991). " Electron Configuration Model, Quantum Mechanics and Reduction". *Br. J. Phil. Sci.* **42** (3): 309–25. ://www.chem.ucla.edu/dept/Faculty/scerri/pdf/BJPS.pdf.

^ [a] [b] Madelung, Erwin (1936). *Mathematische Hilfsmittel des Physikers*. Berlin: Springer.

^ Scerri, Eric R. (1998). " Good Is the Quantum Mechanical Explanation of the Periodic System?". *J. Chem. Ed.* **75** (11): 1384–85. ://www.chem.ucla.edu/dept/Faculty/scerri/pdf/How_Good_is.pdf. Ostrovsky, V.N. (2005). " Recent Discussion Concerning Quantum Justification of the Periodic Table of the Elements". *Foundations of Chemistry* **7** (3): 235–39. doi:.1007/s10698-005-2141-y. ://www.springerlink.com/content/p2rqg32684034736/fulltext.pdf. .

^ Melrose, Melvyn P.; Scerri, Eric R. (1996). " the 4s Orbital is Occupied before the 3d". *J. Chem. Ed.* **73** (6): 498–503. ://jchemed.chem.wisc.edu/Journal/Issues/1996/Jun/jceSubscriber/JCE1996p0498.pdf. .

^ Meek, Terry L.; Allen, Leland C. (2002). " irregularities: deviations from the Madelung rule and inversion of orbital energy levels". *Chem. Phys. Lett.* **362** (5–6): 362–64. doi:.1016/S0009-2614(02)00919-3. ://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6TFN-46G4S5S-1&_user=961305&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000049425&_version=1&_urlVersion=0&_userid=961305&md5=cef78ae6aced8ded250c6931a0842063.

^ International Union of Pure and Applied Chemistry. " effects". *Compendium of Chemical Terminology* Internet edition.

^ Pyykkö, Pekka (1988). "Relativistic effects in structural chemistry". *Chem. Rev.* **88**: 563–94.

Jolly, William L. (1991). *Modern Inorganic Chemistry* (2nd Edition ed.). New York: McGraw-Hill. pp. : 1–23. ISBN 0-07-112651-1.

http://antoine.frostburg

Module 1: Atomic and Molecular orbitals

Unit 2: Pauli exclusion principle and the Hund's rule

Contents

1.0 Introduction 36

2.0 Objectives... 36

3.0 Definitions pauli exclusion principle and Hund's rule 37

  3.1 Pauli exclusion principle... 37

3.2 Hund's Rule 37

3.3.1 Atomic radius 39

3.3.2 Writing electron configurations 45

3.4 Properties of Monatomic Ions 48

4.0 Conclusion 50

5.0 Summary 50

6.0 Tutor marked assignment 51

7.0 Further readings and references 51

1.0 Introduction

The Pauli exclusion principle is a quantum mechanical principle formulated by Wolfgang Pauli in 1925. It states that no two identical fermions may occupy the same quantum state simultaneously. A more rigorous statement of this principle is that, for two identical fermions, the total wave function is anti-symmetric. For electrons in a single atom, it states that no two electrons can have the same four quantum numbers, that is, if n, l, and m_l are the same, m_s must be different such that the electrons have opposite spins.

2.0 Objectives

By the end of this unit, you should be able to:

(a) define Pauli Exclusion Principle and the Hund's rule;

(b) arrange electrons in the atomic orbitals and

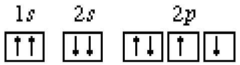
(c) explain the trend in the periodic Table.

3.0 Definitions Pauli exclusion principle and Hund's rule

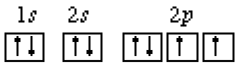
Pauli Exclusion Principle states that no two electrons in the same atom can have the same values for all four quantum numbers. **Hund's Rule** states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin.

3.1 Pauli exclusion principle

An orbital can hold 0, 1, or 2 electrons only, and if there are two electrons in the orbital, they must have opposite (paired) spins. Therefore, no two electrons in the same atom can have the same set of four quantum numbers.



incorrect; electrons must spin in opposite directions



correct; the electrons have opposite spins

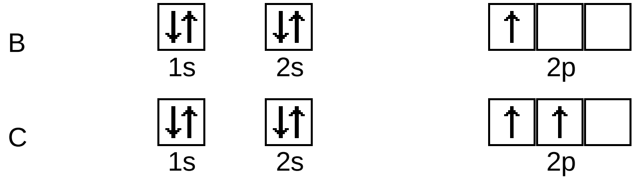
3.2 Hund's Rule

Recall that the Pauli Exclusion Principle states that an orbital may hold a maximum of 2 electrons. Hund's Rule states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin. So, what is this saying and why does it matter? If we look at the **box diagram**, below for the element nitrogen, we see boxes representing orbitals and arrows representing electrons. We add electrons from the bottom up, putting only 2 electrons in each box (one arrow going up and one going down indicate electrons of opposite spin). When we get to the "2p" orbitals, we have 3 separate orbitals in which to place electrons and 3 electrons to place. How are they placed in the orbitals, each of equal energy (distance from the nucleus)? One idea is to place 2 electrons in the first box and one in the second box. Hund's rule, however, says we should place one electron in each box before we start doubling up, so the box diagram for nitrogen shows this. If we had one more electron to place (if we had the next element, oxygen), there would be 2 electrons in the first "2p" orbital.

We can look at Hund's Rule like a house with just as many bedrooms as children. Each child likely wants his own room - they do not double up unless they have to. If a fourth child comes along, then 2 must fit in one bedroom. The other box diagram, below, for Manganese, shows the same situation. There are 5 "d" orbitals and 5 electrons to place. One electron goes in each of the 5 "d" orbitals – two will not be placed in any orbital until each has at least one electron. So why is this big deal? Recall that electrons have a "spin" and therefore are like little magnets. If an element has many unpaired electrons, a sample of it can become magnetic if all of the atoms in the sample are oriented properly. We see this most commonly with the elements iron, cobalt and nickel. All three have unpaired electrons in their "d" orbitals and if oriented properly, large samples of these elements can become a magnet. Most magnets you are familiar with are made of iron.

Examples of ground state electron configurations in the orbital box notation that shows electron spins.

atom orbital box diagram



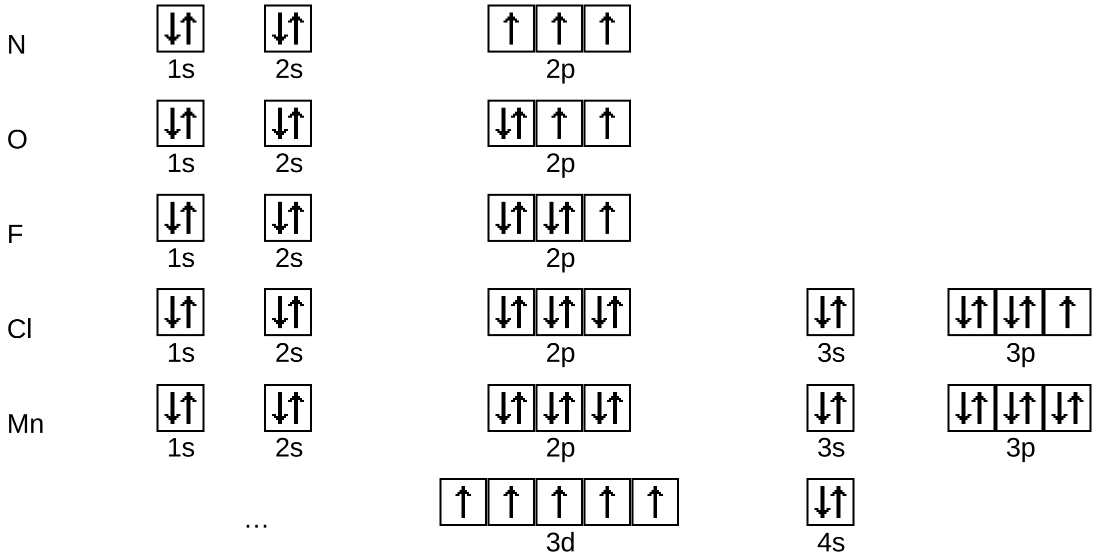


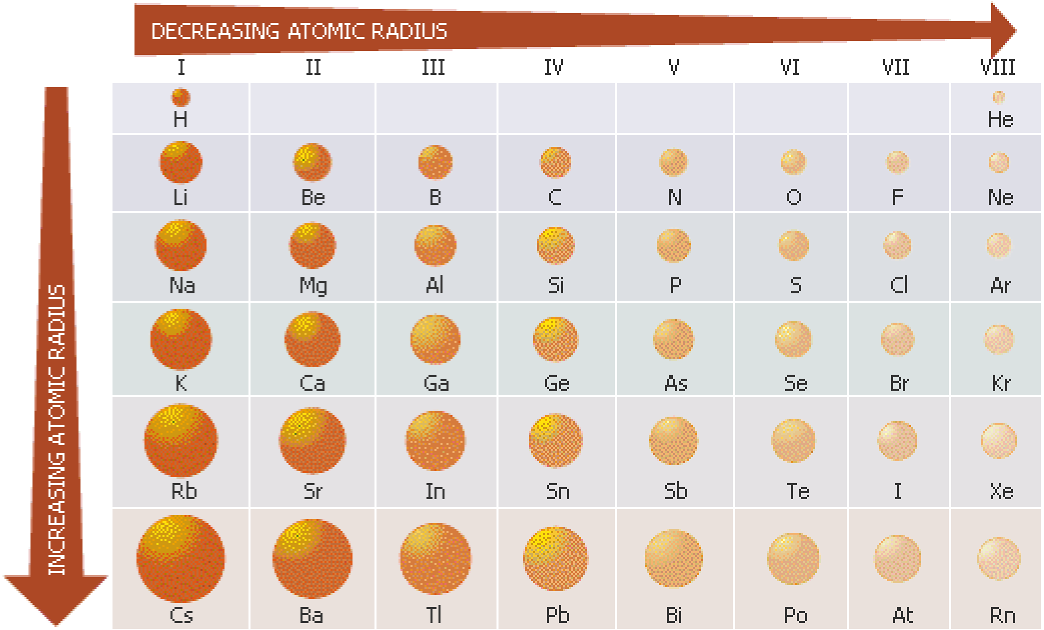
Figure 1.2.1: Filling of orbitals of elements according to Pauli Exclusion Principle and Hund's Rule.

***Source*:** General Chemistry Online (http://antoine.frostburg.edu/chem/senese/101/electrons/index.shtml)

3.3 Trends and the Periodic table

3.3.1 Atomic radius

Now that we have a pretty good handle on electron configurations and their relationship to the periodic table, we can look at a couple of trends that are important. The first one is **atomic size or atomic radius**. As we go down any group on the periodic table, the atoms (and the ions they form when they gain or lose electrons) get larger. Why? Because as we go down a group, we have electrons in higher and higher energy levels which are farther away from the nucleus. The electron distance from the nucleus determines the size of the atom. If we go across a period, however, the atoms get smaller. This is curious since as we go across a period, we are adding electrons, just like we did going down a group. But, the electrons we are adding are all in the same principal energy level and therefore not any farther away from the nucleus. At the same time, the numbers of protons are increasing as we go across a period.



Ionization Energy

Figure 1.2.2: Variation of atomic radii with ionization energy in elements.

***Source*: www.asd.k12.ak.us/hauser**

This increases the positive charge in the atom which pulls the electrons in closer towards the nucleus. So, as we go across a period on the periodic table, the atoms (and the ions they form when they gain or lose electrons) get smaller.

When an atom gains enough energy to not just excite its electrons to higher energy levels, but to remove an electron completely, it has absorbed the atom's **ionization energy**. Remember when we discussed Bohr's model of the atom with a rubber band. As we pull the rubber band away from a finger, the electron is gaining energy. If we pull the rubber band hard enough it may break free completely. If this happens, the atom we are modeling has become an **ion**. We have given an atom its ionization energy. If we consider this ionization energy in relation to the elements on the periodic table, we can also see some trends. As we go down a vertical column (a group or family), the valence electrons are farther and farther away from the grip of the nucleus. It gets easier and easier to pull one electron away to make an ion. So, we say that ionization energy decreases as we go down a group. As we go across a row of the periodic table (a period), the electrons are not really any farther away from the nucleus since they are all in the same principal energy level. But, the positive charge in the nucleus in increasing since more and more protons are being added, so it becomes harder and harder to pull one electron away. So, we say that ionization energy increases as we go across a period. This idea becomes important as we consider an atom's reactivity. The easier it is to pull away an electron from a metal atom, the more reactive the metal is and the more likely it will want to combine with a nonmetal element to form a compound. Metals have tendency to lose electrons to form positive ions (**cations**) and nonmetals have tendency to gain electrons to form negative ions (**anions**). This will be the basis for the next unit on chemical bonding.

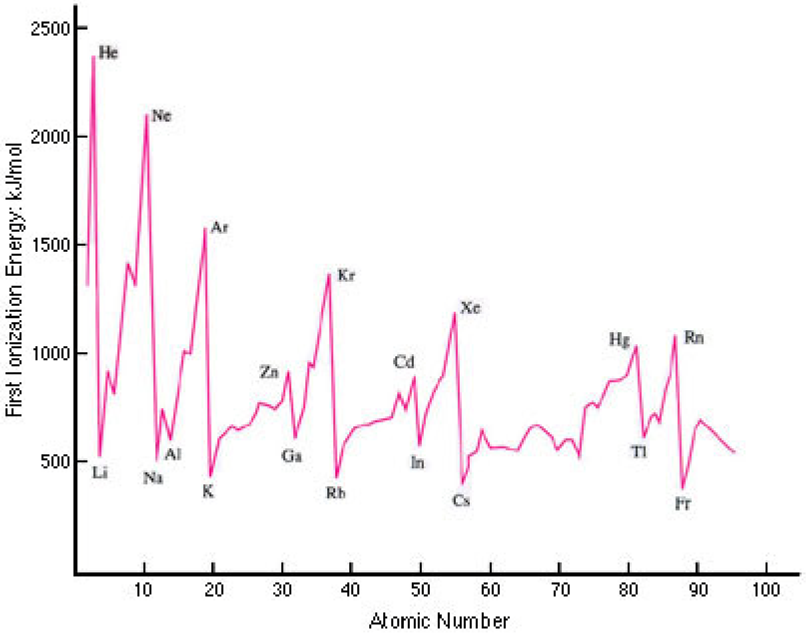


Figure 1.2.3: Variation of ionization energy with atomic number in elements

Source**:** **www.asd.k12.ak.us/hauser**

So, this long unit on light and where the electrons reside in the atom has given us the basis we need for describing how and why atoms behave the way they do and the mechanism for atoms combining to form compounds. Each electron in an atom is described by four different **quantum numbers**. The first three (n, l, m_l) specify the particular orbital of interest, and the fourth (m_s) specifies how many electrons can occupy that orbital.

1. **Principal Quantum number (n): $n = 1, 2, 3\ldots \infty$**

   Specifies the **energy** of an electron and the **size** of the orbital (the distance from the nucleus of the peak in a radial probability distribution plot). All orbitals that have the same value of n are said to be in the same **shell** (**level**). For a hydrogen atom with n=1, the electron is in its *ground state*; if the electron is in the $n = 2$ orbital, it is in an *excited state*. The total number of orbitals for a given n value is n^2.

2. **Angular momentum (Secondary, Azimunthal) Quantum number (l): $l = 0, ..., n-1$.**

   Specifies the **shape** of an orbital with a particular principal quantum number. The secondary quantum number divides the shells into smaller groups of orbitals called **subshells** (**sublevels**). Usually, a letter code is used to identify l to avoid confusion with n:

l	0	1	2	3	4	5	...
Letter	*s*	*p*	*d*	*f*	*g*	*h*	...

The subshell with $n = 2$ and l=1 is the 2*p* subshell; if $n = 3$ and $l = 0$, it is the 3*s* subshell, and so on. The value of l also has a slight effect on the energy of the subshell; the energy of the subshell increases with l ($s < p < d < f$).

3. **Magnetic Quantum number (m_l): $m_l = -l, ..., 0, ..., +l$.**

   Specifies the **orientation in space** of an orbital of a given energy (n) and shape (l). This number divides the subshell into individual **orbitals** which hold the electrons; there are $2l+1$ orbitals in each subshell. Thus the *s* subshell has only one orbital, the *p* subshell has three orbitals, and so on.

4. **Spin Quantum number (m_s): m_s = +½ or -½.**

   Specifies the **orientation of the spin axis** of an electron. An electron can spin in only one of two directions (sometimes called *up* and *down*).

   The **Pauli exclusion principle** (Wolfgang Pauli, Nobel Prize 1945) states that *no two electrons in the same atom can have identical values for all four of their quantum numbers*. What this means is that no more than **two** electrons can occupy the same orbital, and that two electrons in the same orbital must have **opposite spins**.

   Because an electron spins, it creates a magnetic field, which can be oriented in one of two directions. For two electrons in the same orbital, the spins must be opposite to each other; the spins are said to be **paired**. These substances are not attracted to magnets and are said to be **diamagnetic**. Atoms with more electrons that spin in one direction than another contain **unpaired** electrons. These substances are weakly attracted to magnets and are said to be **paramagnetic**.

Table of Allowed Quantum Numbers

N	***l***	**m_l**	**Number of orbitals**	**Orbital name**	**Number of electrons**
1	0	0	1	1*s*	2
2	0	0	1	2*s*	2

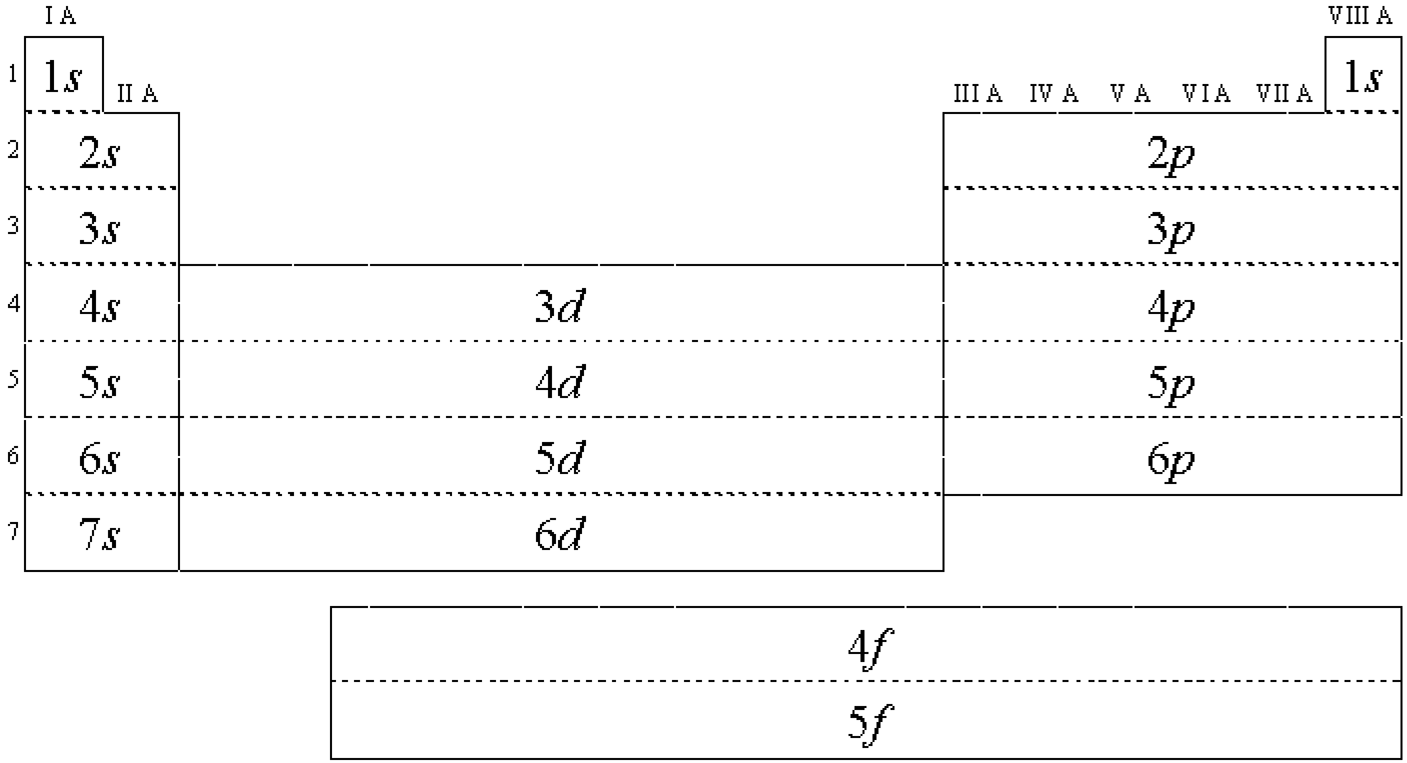
	1	-1, 0, +1	3	2*p*	6
3	0	0	1	3*s*	2
	1	-1, 0, +1	3	3*p*	6
	2	-2, -1, 0, +1, +2	5	3*d*	10
4	0	0	1	4*s*	2
	1	-1, 0, +1	3	4*p*	6
	2	-2, -1, 0, +1, +2	5	4*d*	10
	3	-3, -2, -1, 0, +1, +2, +3	7	4*f*	14

3.3.2 Writing electron configurations

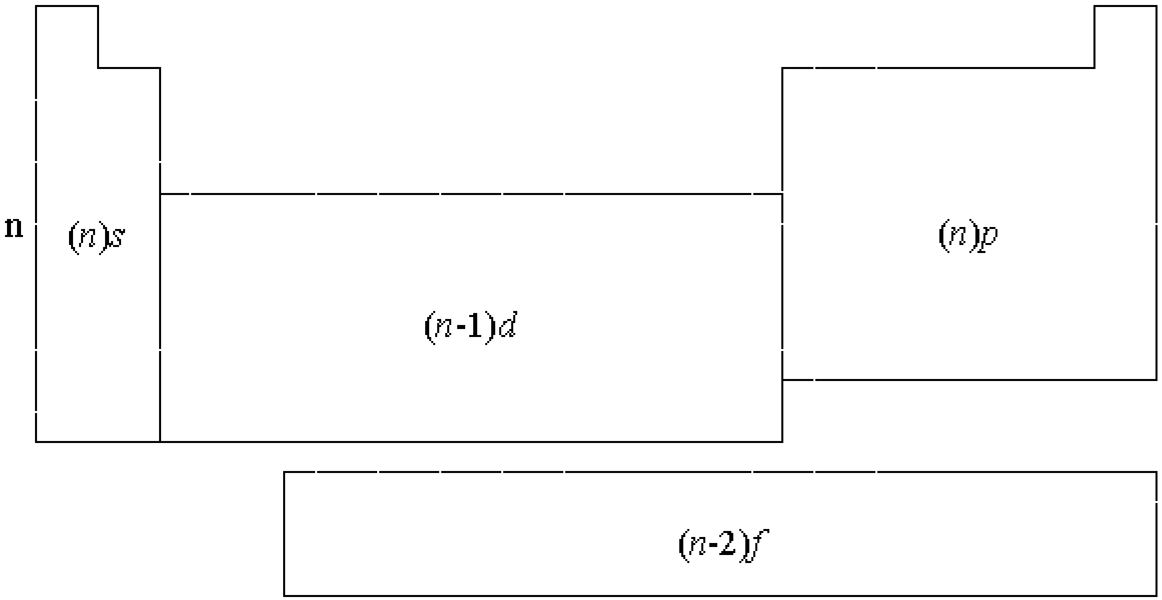
The distribution of electrons among the orbitals of an atom is called the **electron configuration**. The electrons are filled in according to a scheme known as the **Aufbau principle** ("building-up"), which corresponds (for the most part) to increasing energy of the subshells:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f

In electron configurations, write in the orbitals that are occupied by electrons, followed by a superscript to indicate how many electrons are in the set of orbitals (e.g., H $1s^1$). It is not necessary to memorize this listing, because the order in which the electrons are filled in can be read from the periodic table in the following fashion:



Or, to summarize:



Source: Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change, 2nd ed.* Boston: McGraw-Hill, 2000, p. 277-284, 293-307.

Another way to indicate the placement of electrons is an **orbital diagram**, in which each orbital is represented by a square (or circle), and the electrons as arrows pointing up or down (indicating the electron spin). When electrons are placed in a set of orbitals of equal energy, they are spread out as much as possible to give as few paired electrons as possible (**Hund's rule**).

In a **ground state** configuration, all of the electrons are in as low an energy level as it is possible for them to be. When an electron absorbs energy, it occupies a higher energy orbital, and is said to be in an **excited state**.

3.4 Properties of monatomic ions

The electrons in the *outermost shell* (the ones with the highest value of *n*) are the most energetic, and are the ones which are exposed to other atoms. This shell is known as the **valence shell**. The inner, *core* electrons (*inner shell*) do not usually play a role in chemical bonding.

Elements with similar properties generally have similar outer shell configurations. For instance, we already know that the alkali metals (Group I) always form ions with a +1 charge; the "extra" s^{1} electron is the one that's lost:

IA	Li	$1s^{2}2s^{1}$	Li+	$1s^{2}$
	Na	$1s^{2}2s^{2}2p^{6}3s^{1}$	Na+	$1s^{2}2s^{2}2p^{6}$
	K	$1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{1}$	K+	$1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}$

The next shell down is now the outermost shell, which is now full — meaning there is very little tendency to gain or lose more electrons. The ion's electron configuration is the same as the nearest noble gas — the ion is said to be **isoelectronic** with the nearest noble gas. Atoms "prefer" to have a filled outermost shell because this is more electronically stable.

- The Group IIA and IIIA metals also tend to lose all of their valence electrons to form cations.

IIA	Be	$1s^{2}2s^{2}$	Be^{2+}	$1s^{2}$
	Mg	$1s^{2}2s^{2}2p^{6}3s^{2}$	Mg^{2+}	$1s^{2}2s^{2}2p^{6}$
IIIA	Al	$1s^{2}2s^{2}2p^{6}3s^{2}3p^{1}$	Al3+	$1s^{2}2s^{2}2p^{6}$

- The Group IV and V metals can lose either the electrons from the *p* subshell, or from both the *s* and *p* subshells, thus attaining a **pseudo-noble gas configuration**.

IVA	Sn	$[Kr]4d^{10}5s^25p^2$	Sn^{2+}	$[Kr]4d^{10}5s^2$
			Sn^{4+}	$[Kr]4d^{10}$
	Pb	$[Xe]4f^{14}5d^{10}6s^26p^2$	Pb^{2+}	$[Xe]4f^{14}5d^{10}6s^2$
			Pb^{4+}	$[Xe]4f^{14}5d^{10}$
VA	Bi	$[Xe]4f^{14}5d^{10}6s^26p^3$	Bi^{3+}	$[Xe]4f^{14}5d^{10}6s^2$
			Bi^{5+}	$[Xe]4f^{14}5d^{10}$

- The Group IV - VII non-metals gain electrons until their valence shells are full (8 electrons).

IVA	C	$1s^22s^22p^2$	C4-	$1s^22s^22p^6$
VA	N	$1s^22s^22p^3$	N3-	$1s^22s^22p^6$
VIA	O	$1s^22s^22p^4$	O2-	$1s^22s^22p^6$
VIIA	F	$1s^22s^22p^5$	F-	$1s^22s^22p^6$

- The Group VIII noble gases already possess a full outer shell, so they have no tendency to form ions.

VIIIA	Ne	$1s^22s^22p^6$

Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

- Transition metals (B-group) usually form +2 charges from losing the valence s electrons, but can also lose electrons from the highest d level to form other charges.

B-group Fe $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ Fe^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

Fe^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Activity A

1. Define each of the following: (a) Pauli exclusion principle (b) Hund's rule;

4.0 Conclusion

For electrons in a single atom, no two electrons can have the same four quantum numbers, that is, if n, l, and m_l are the same, m_s must be different such that the electrons have opposite spins.

5.0 Summary

In this unit, we have learnt that:

(i) Pauli exclusion principle states that an orbital may hold a maximum of 2 electrons;

(ii) Hund's rule states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron, and all electrons in singly occupied orbitals must have the same spin;

(iii) As we go down any group on the periodic table, the atoms (and the ions they form when they gain or lose electrons) get larger;

(iv) ionization energy decreases as we go down a group;

(v) ionization energy increases as we go across a period.

6.0 Tutor marked assignment (TMA)

1. Write the electronic configuration of the first 10 elements in the periodic Table.
2. Explain the trend of ionization energy in the periodic Table.

7.0 Further readings and references

Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change, 2nd ed.* Boston: McGraw-Hill, 2000, p. 277-284, 293-307

http://www2.asd.k12.ak.us/hauser/curriculum/html/Chemistry/Unit Modern Atomic Theory/Handouts and0Notes/Unit_09_Light_(Handout).htm

Babarinde, A. (2009) Introduction to Quantum Chemistry. Lucky Odoni Publishers, Ijebu-Ode, ISBN 978-178-212-9

General Chemistry Online http://antoine.frostburg.edu/chem/senese/101/electrons/index.shtml

Module 1: Atomic and molecular orbitals

Unit 3: Molecular orbitals of molecules

Contents

1.0 Introduction 53

2.0 Objective 54

3.0 Definition of molecular orbital 54

3.1 MO description of homonuclear diatomic molecules 54

3.2 Bond order 57

3.3 Some important consequence from molecular orbital theory 57

3.4 Molecular orbital theory of heteronuclear diatomic molecules 58

3.4.1 Hydrogen fluoride 58

3.4.2 Huckel theory: Bonding in polyatomic molecules 59

4.0 Conclusion 60

5.0 Summary 60

6.0 Tutor marked assignment (TMA) 61

7.0 Further reading and references 61

1.0 Introduction

Molecular orbitals are usually constructed by combining atomic orbitals or hybrid orbitals from each atom of the molecule, or other molecular orbitals from groups of atoms. A molecular orbital (MO) can be used to specify the electron configuration of a molecule: the spatial distribution and energy of one (or one pair of) electron(s). Most commonly a MO is represented as a linear combination of atomic orbitals (the LCAO-MO method); especially in qualitative or very approximate usage. They are invaluable in providing a simple model of bonding in molecules, understood through molecular orbital theory. Most methods in computational chemistry today start by calculating the MOs of the system. A molecular orbital describes the behavior of one electron in the electric field generated by the nuclei and some average distribution of the other electrons. In the case of two electrons occupying the same orbital, the Pauli exclusion principle demands that they have opposite spin. Necessarily this is an approximation, and highly accurate descriptions of the molecular electronic wave function do not have orbitals.

2.0 Objectives

By the end of this Unit, you should be able to:

(a) define molecular orbital;
(b) explain how molecular orbital are formed;
(c) give the consequence from molecular orbital theory and
(d) use bond order to determine the possibility of bond formation in molecules.

3.0 Definition of molecular orbital

In chemistry, a molecular orbital (MO) is a mathematical function that describes the wave-like behavior of an electron in a molecule. This function can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region. The use of the term "orbital" was first used in English by Robert S. Mulliken in 1925 as the English translation of Schrödinger's use of the German word, 'Eigenfunktion'. It has since been equated with the "region" generated with the function. They can be quantitatively calculated using the Hartree-Fock or Self-Consistent Field method.

3.1 Molecular orbital (MO) description of homonuclear diatomic molecules

In this section the molecular orbital description of homonuclear diatomic molecules will be discussed. In the first approximation only the atomic orbitals having similar energy will combine to form the MO. In this approximation the simplest way to form molecular orbital is to combine the corresponding orbitals on two atoms (i.e. 1s + 1s, 2s + 2s, etc.). The appropriate combinations are

$\sigma(1s) = 1s_A + 1s_B$

$\sigma(1s)^* = 1s_A - 1s_B$

$\sigma(2s) = 2s_A + 2s_B$

$\sigma(2s)^* = 2s_A - 2s_B$

$\sigma(2p) = 2p_{xA} + 2p_{xB}$

$\sigma(2p)^* = 2p_{xA} - 2p_{xB}$

$\prod(2p_y) = 2p_{yA} + 2p_{yB}$

$\prod(2p_z) = 2p_{zA} + 2p_{zB}$

$\prod(2p_y)^* = 2p_{yA} - 2p_{yB}$

According to this approximation the 1s orbitals from two different atoms will form $\sigma_g(1s)^*$ and $\sigma_u(1s)^*$ just like the MO's of hydrogen molecule. In the similar way 2s

orbitals from two different atoms will form $\sigma_g(2s)^*$ and $\sigma_u(1s)^*$ MO. These two molecular orbitals will look like $\sigma_g(2s)$ and $\sigma_u(2s)^*$. Since an atomic 2s orbital has higher energy than atomic 1s orbital $\sigma_g(2s)$ and $\sigma_u(2s)^*$ MO will have higher energy in comparison to $\sigma_g(2s)$ and $\sigma_u(2s)^*$ MO respectively. So the ordering of the molecular orbitals discussed so far will be $\sigma_g(2s) < \sigma_u(2s)^* < \sigma_g(2s) < \sigma_u(2s)^*$. Now let us discuss about the combination of the 2p orbitals. Except hydrogen atom 2p orbital energy is higher than the 2s orbital energy; the bonding and antibonding molecular orbital formed from the combination of 2p orbital will have higher energy than $\sigma_g(2s)$ and $\sigma_u(2s)^*$ respectively. If we consider the x axis as molecular axis then these two orbitals will be denoted as $\sigma_g(2p)$ and $\sigma_u(2p)^*$.The remaining 2p orbitals i.e. $2p_y$, and $2p_z$ will form Π molecular orbitals by lateral overlapping. The bonding and antibonding molecular orbital forming by overlapping $2p_y$ orbitals are denoted $\Pi_u(2p_y)$ and $\Pi_g(2p_y)^*$ .These two orbital will be directed towards Y axis. The $2p_z$ combined in the similar manner will result in bonding and antibonding Π MO but these will be directed along the Z axis.

The bonding Π orbitals arising from the combination of two $2p_y$ atomic orbitals and two $2p_z$ will degenerate and similarly the antibonding Π^* MOs. Now to determine the electron configuration of molecule by placing the electrons in these MOs in accord to the Pauli's exclusion principle and Hund's rule just like multi-electronic atoms, we need to know the energy ordering of these molecular orbitals. The energy of the molecular orbitals depends on the atomic number (atomic charge) on the nuclei. As the atomic number increases from lithium to fluorine, the energy of the $\sigma_g(2p)$ and energy of $\Pi_u(2p_y)$ and $\Pi_u(2p_z)$ orbitals approaches to each other

and interchange order in going from N_2 and O_2 .

But in case of N_2 molecule the MO diagram, the energy of the $\sigma_g(2p)$ orbital will be less than that of $\Pi_u(2p_y)$ and $\Pi_u(2p_z)$ orbitals .

3.2 Bond order

The net bonding in a diatomic molecule is defined by a quantity called bond order, b;

$b = {}_{2}(n - n^*)$ (13.9)

Where n is the number of electron in the bonding orbital and n* is the number of electrons in the antibonding orbital. This is a very useful quantity for describing the characteristics of bonds, because it correlates with bond length and bond strength. If the bond order between atoms of a given pair of elements is higher then the bond length will be shorter and consequently the bond will be stronger. The bond strength is measured by bond dissociation energy which is the energy required to separate the atoms to infinity. Single bonds have bond order one; double bonds have two; and so on. The bond order zero indicates that there is no bond between the given pair of atoms. For example bond order for He_2 is zero, because there are two electrons in both bonding and antibonding orbital. For this reason He_2 molecule does not exist.

3.3 Some important consequence from molecular orbital theory

3.3.1 Prediction whether a molecule exists or not: From MO theory we can predict whether a diatomic molecule exists or not by simply calculating the bond order. If the value is greater than zero the molecule will exist. For example the ground state electronic configuration of He_2^+ is $\sigma(1s)\ {}_{2}\sigma(1s)_{*2}$, and the bond order is 0.5 . So He_2^+ ion exists but since the bond order of the He_2 molecule is zero it will not exist.

Lithium and beryllium molecules: The six electrons from two lithium atoms will fill in the molecular orbital according to Aufbau principle. Four will fill in the $\sigma_g(1s)$ and $\sigma_g(1s)_*$ with no bonding. The last two electrons will enter in the $\sigma_g(2s)$ orbital. Hence the bond order in the lithium molecule will be one and the electronic configuration will be KK $\sigma_g(2s)_2$

where K stands for the K (1s) shell. The electronic configuration of beryllium molecule will be

KK $\sigma(2s)^2\ \sigma(2s)^{*2}$.

Since the number of electrons in the bonding and anti-bonding molecular orbital is equal, the bond order will be zero. Hence like diberilium molecule (Be_2) molecule does not exist. Experimentally it is found that lithium is diatomic and beryllium is mono-atomic in the gaseous phage.

3.3.2 Paramagnetic property of oxygen molecule: One of the most impressive successes of the molecular orbital theory is the prediction of correct electronic configuration of oxygen molecule. The experimental result shows that the oxygen molecule is paramagnetic, the net spin of oxygen molecule corresponds to two unpaired electron having same spin. According to molecular theory the ground state of oxygen molecule is KK $\sigma(2s)_2\ \sigma(2s)^{*2}\ \sigma(2p_x)^2\ \Pi(2p_y)^2 \Pi\ (2p_z)^2\ \Pi(2p_y)^1 \Pi(2p_z)^1$. According to Hund's rule two electrons having parallel spin will occupy two degenerate $\Pi\ (2p_y)$ and $\Pi\ (2p_z)$ orbital. This explains the magnetic behavior of oxygen molecule.

3.4 Molecular orbital theory of heteronuclear diatomic molecules

Since in this case the energies of the atomic orbital (AO) on the two atoms from which the molecular orbital are formed are different, the combination of atomic orbital to form molecular orbital will be different from that in the case of homo-nuclear diatomic molecules. In order to develop the molecular orbital description of hetero nuclear diatomic molecule we need to consider the fact that different types of atoms have different capacities to attract the electrons. So basically the electronegativity of the bonded atoms plays vital role in the treatment of hetero-nuclear bond. The bonding electron will be more stable in the presence of the nuclei of the atom having greater electronegativity, i.e. the atom having lower energy. Probability of finding the bonded electrons will be more near that nucleus. The electron cloud will be distorted towards that nucleus and hence the MO will resemble that AO more than the AO on the less electronegative atom. This description can easily describe the polarity of the hetero-nuclear molecules.

3.4.1 Hydrogen fluoride

Hydrogen fluoride is a simple hetero-nuclear diatomic molecule. Since the electronegativity of fluorine atom is much higher than that of hydrogen atom, the energy of 1s orbital of hydrogen atom is much higher than the atomic orbital of fluorine atom. The molecular orbital will be formed due the combination of hydrogen 1s orbital with 1s, 2s and 2p orbitals of fluorine. The pictorial representation of the MO diagram is given fig18. There are eight valence electrons which occupy four molecular orbitals. The two highest energy MO's are degenerate, are π-type formed only from two 2p orbitals of fluorine atom and hence have no electron density associated with the hydrogen atom, *ie*. they are Non-Bonding Orbitals (**NBO**). In Lewis theory these two electrons are represented as two "*Lone Pairs*". We can see from the MO diagram that the electron density is not equally distributed about the molecule. There is a much greater electron density around the fluorine atom because of extremely electronegativity of fluorine atom, and in each bonding molecular orbital, fluorine will take a greater share of the electron density.

3.4.2 Huckel theory: Bonding in polyatomic molecules

In case of polyatomic molecules the combinations among the atomic orbitals are complicated. One widely used approximated theory to describe the molecular orbitals in polyatomic molecule is Huckel molecular theory (HMO). Huckel MO theory is based on the treatment of Π electrons in conjugated molecules. Here Π orbitals are treated separately from the σ orbitals which give the framework of the molecule. The Π electron Hamiltonian is simply written as a sum of one-electron terms. It follows that the total energy is the sum of one-electron energies. The sum is over all electrons. Since each molecular orbital is doubly occupied (for a normal closed shell hydrocarbon, which is the class we shall restrict ourselves to for now), this is twice the sum of energy terms for each molecular orbital. Each molecular orbital $_i$ is now described as a linear combination of atomic orbitals. Now the next task is to calculate the coefficient of the atomic orbitals to find out the molecular orbitals and their energies.

Let us illustrate the theory with the example of ethene:

The number of atoms (i.e. C atoms) (*n*) is 2, so the molecular orbitals are of the form:

Since there are two atomic orbitals, two molecular orbitals, will formed due to the combination of the orbitals, one will be bonding and other will be antibonding. The electrons will in the bonding orbital of the system. Note that each C atom always contribute one electron to the system for a neutral hydrocarbon, so the number of electrons is then equal to the number of atoms, and the number of occupied orbitals (m) is $n/2$.

The best molecular orbitals are those which give the minimum total energy. The details of the procedure is beyond the scope of this study material.

Activity

Define molecular orbital and give the appropriate combinations of the atomic orbitals.

4.0 Conclusion

Molecular orbitals are usually obtained from the combination of atomic orbitals or hybrid orbitals.

5.0 Summary

In this unit, we have learnt that;

- **(i)** molecular orbital (MO) is a mathematical function that describes the wave-like behavior of an electron in a molecule.
- **(ii)** the wavefunction can be used to calculate chemical and physical properties such as the probability of finding an electron in any specific region.
- **(iii)** the net bonding in a diatomic molecule is defined by a quantity called bond order.

6.0 Tutor marked assignment (TMA)

1. explain how molecular orbital are formed.
2. give the consequence from molecular orbital theory and
3. use bond order to determine the possibility of bond formation in the following molecules: (a) Li_2 (b) Be_2 (c) He_2 (d) O_2

7.0 Further reading and references

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/mo.php

Babarinde, A. (2009) Introduction to Quantum Chemistry. Lucky Odoni Publishers, Ijebu-Ode, ISBN 978-178-212-9

Module 1: Atomic and Molecular orbitals

Unit 4: Atomic spectra

Contents

1.0 Introduction 62

2.0 Objectives 63

3.0 Definition of Atomic spectra 63
  3.1 Line spectra of atoms 63
  3.2 The Spectrum of atomic hydrogen 66
4.0 Conclusion 69
5.0 Summary 69
6.0 Tutor marked assignment (TMA) 70
7.0 Further reading and references 70

1.0 Introduction

When an element is heated in a flame or a discharge of electricity is passed through a gas, colours of light characteristic of the element are seen. For example, discharge tubes containing neon gas at low pressure glow red, sodium light emits yellow light and mercury gives a green glow.

2.0 Objectives

By the end of this Unit, you should be able to:

(a) define atomic spectra;

(b) explain the origin of atomic spectra;

(c) calculate the wavelength in the atomic spectra of hydrogen and

(d) explain the five series for atomic spectra of hydrogen.

3.0 Definition of Atomic spectra

When the light generated from the element by heating or from a gas as a result of the passage of electricity is passed through a spectroscope it produces a spectrum known as emission spectrum. The emission spectrum that is produced consists of a series of lines, called line spectrum or atomic spectrum. Each element gives a unique pattern of spectra lines, and each line has a distinct wavelength. The atomic spectra of the elements heavier than hydrogen are considerably more complex.

3.1 Line spectra of atoms

The radiation produced from elemental emission consists of a complex mixture of wavelengths which can be dispersed into its various individual components by means of a spectrometer. The result of such a measurement yields an emission spectrum which is a plot of the intensity of the emitted radiation as a function of wavelength or another related variable. The spectra of atoms in the gas phase consist of a number of sharp lines. In the case of atomic hydrogen, the spectrum is very simple. The occurrence of atomic as well as molecular line spectra provides resounding evidence that the energies of atoms and molecules must be quantized rather than continuous. When the element or gas is heated to produce the spectrum, the atoms of the element or gas become more energetic. They are consequently promoted to the excited state. After a while, the added energy can be re-emitted in the form of photons as the atom return to the ground state, thereby giving rise to the observed emission spectrum. In a normal gas sample made up of large number of molecules, each atom would take an arbitrary amount of energy. This will form a continuous distribution of energies the result of which would be continuous radiation spectrum. However, the observed spectra are made up of sharp lines, which imply that the energies of the atoms and molecules responsible for such lines must be discrete rather than continuous.

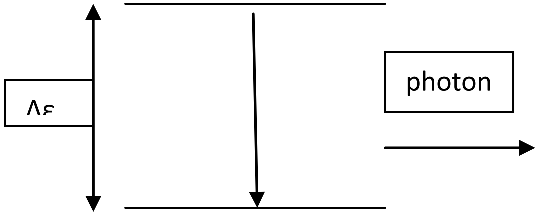


Figure 1.4.1: The representation of an atom with energy levels that have an energy difference (Δε)
Source: University Chemistry

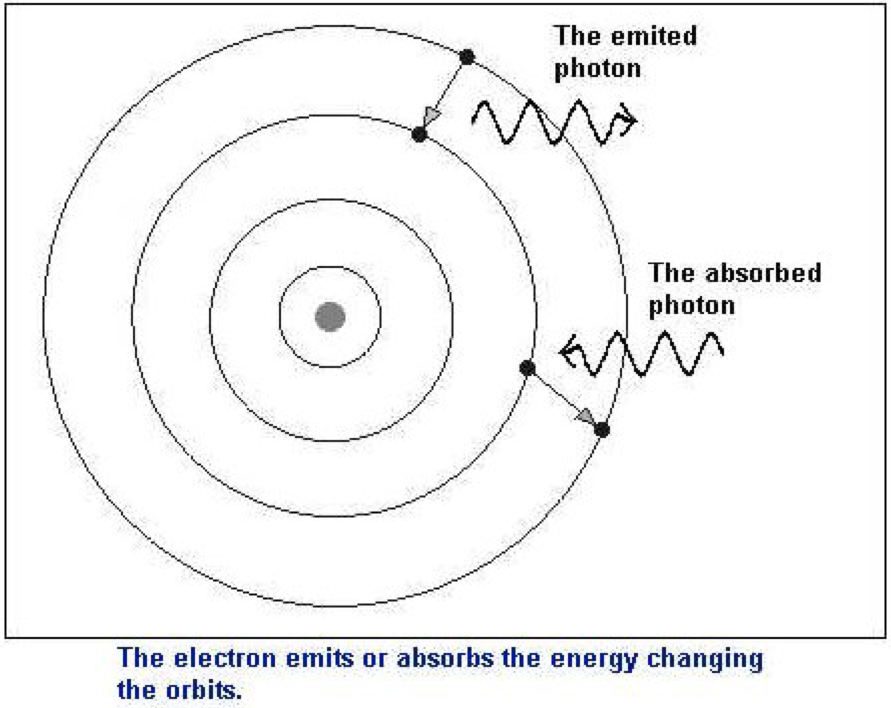


Figure 1.4.2 The absorption and emission of energy by electron

***Source*: Dr Sourav Pal, Dept of Physical Chemistry, National chemical Laboratory, India**

When an electron in the excited state makes a transition to ground state the energy is emitted in the form of radiation of energy. Atoms are said to possess energy levels because they can only possess discrete amount of energy. The lowest energy level is known as the *ground state* while the energy levels above the ground state are referred to as the *excited states*.

Absorption of energy makes atomic electron jump from the ground state to the excited state. On transition back to the ground state, the energy earlier absorbed is released in form of emitting a photon. By the law of conservation of energy, the energy loss by the atom in transition from excited back to the ground state must be equal to the energy of the photon. This gives us the fundamental formula of spectroscopy (equation (1.6.1)).

$$\Delta\varepsilon = \varepsilon_\gamma = h\nu = hc/\lambda \qquad \text{………………………} \quad (1.4.1)$$

This equation shows the relation between wavelength of the observed emitted light and the energy difference between the ground and excited states of the atom.

3.2 The Spectrum of atomic Hydrogen

Niel’s Bohr developed the concept of quantization of energy levels in electrons in atoms in his explanation of the spectrum of atomic hydrogen. Atomic hydrogen has only one electron hence the simple nature of the emission spectrum for it. It displayed several lines in the visible, infrared and the ultraviolet regions. The observed spectra lines are well fitted by the empirical Rydberg formula

$$\bar{\nu} = 1/\lambda = \Re[((1/n_2^2)-(1/n_1^2)] \qquad \text{………………………} \quad (1.4.2)$$

where n_1 and n_2 are integers($n_1 > n_2$), and $\Re$ is the Rydberg’s constant , with a value of

$\Re = 1.097 \times 10^5$ cm^{-1}.The spectrum of atomic hydrogen have all lines belonging to a given series with a common value of n_2 but different values of n_1. On the basis of this there are five series each having the value of n_2 as shown in Table 1.6.1.

Table 1.4.1 The series in the spectrum of atomic hydrogen

Series	n_2	n_1	Region in electromagnetic spectrum	Wavelength (nm)
Lyman	1	2,3,4,5 …	Ultraviolet	121.6
Balmer	2	3,4,5,6 …	Visible	656.3
Paschen	3	4,5,6,7 …	Infrared	1875
Brackett	4	5,6,7,8 …	Infrared	4051
Pfund	5	6,7,8,9 …	Infrared	7458

Source: Modern University Chemistry

Example

Calculate the wavelength of the visible line in the hydrogen spectrum that has the longest wavelength. What is the energy difference between the two levels of the atom involved in the transition giving rise to this line?

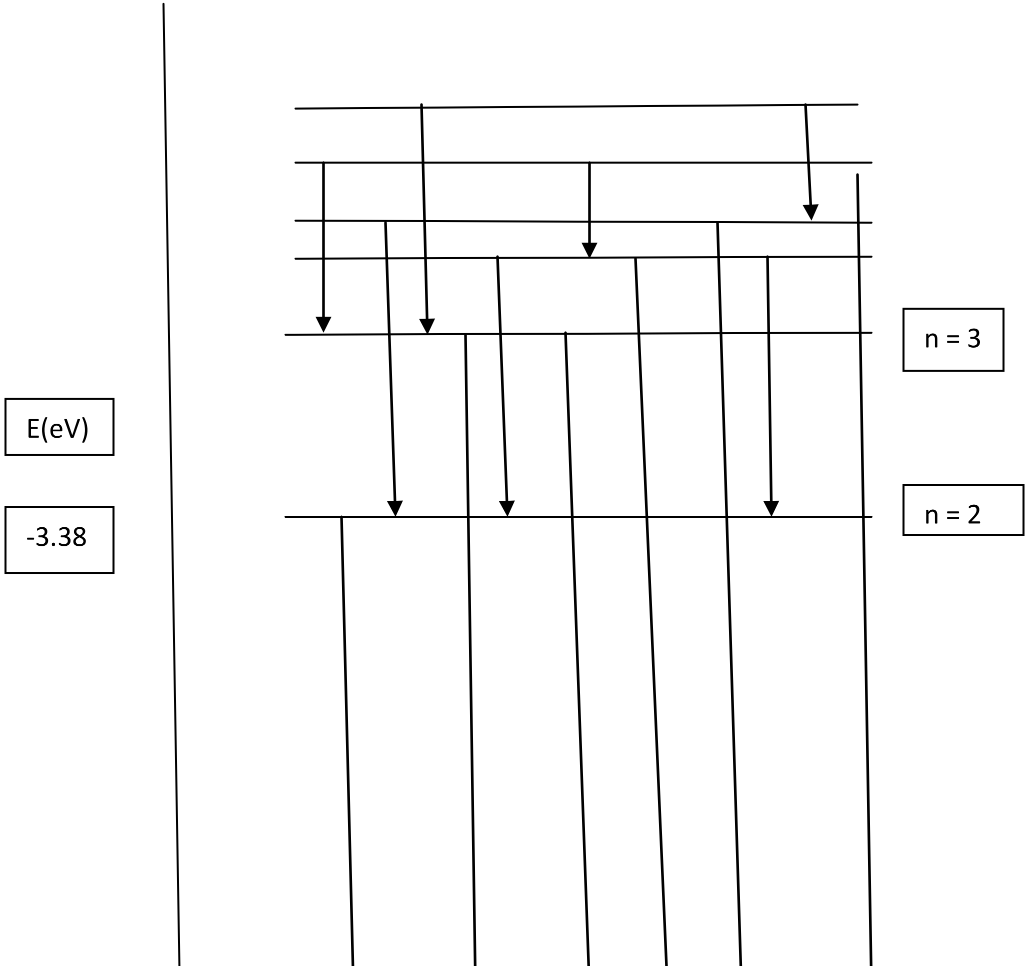
Visible line means that $n_2 = 2$ of the Balmer series which lies in the visible region of the electromagnetic spectrum. Transition can only be from $n_2 = 2$ to $n_1 = 3, 4, 5, ….$ The longest wavelength corresponds to the lowest energy difference since wavelength is inversely proportional to energy of the photon emitted. The lowest energy difference means that the transition should be between level n_2 =2 and level n_1 = 3.

Using Rydberg's formula

$\nu = 1/\lambda = \Re[((1/n_2^2)-(1/n_1^2)]$

$= 1.097 \times 10^5 \text{ cm}^{-1} [(1/2^2) - (1/3^2)]$

$\lambda = 1/\nu = 656.3$ nm



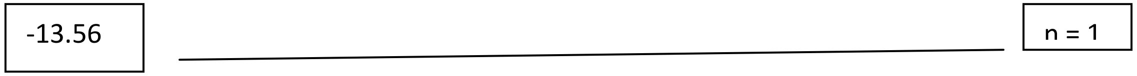


Figure 1.4.2: Energy level diagram of the hydrogen atom with vertical arrows showing various electronic transitions between different levels and the spectral series to which they belong.

Source: Modern University Chemistry

Activity A

The electron in a hydrogen atom is excited to the n = 4 level. Calculate the wavelengths of all the photons that can be emitted as the electron returns to the ground state.

4.0 Conclusion

The occurrence of atomic as well as molecular line spectra provides resounding evidence that the energies of atoms and molecules must be quantized rather than continuous.

5.0 Summary

In this unit we have learnt that:

The radiation produced from elemental emission consists of a complex mixture of wavelengths which can be dispersed into its various individual components by means of a spectrometer.

(i) the observed spectra are made up of sharp lines, which imply that the energies of the atoms and molecules responsible for such lines must be discrete rather than continuous.

(ii) atomic hydrogen has only one electron hence the simple nature of the emission spectrum for it.

6.0 Tutor marked assignment (TMA)

1. What are the wavelengths of the three Paschen lines of hydrogen having (a) the lowest frequencies (b) second to the lowest frequencies?
2. The electron in a hydrogen atom is excited to the n = 5 level. Calculate the wavelengths of all the photons that can be emitted as the electron returns to the ground state.

7.0 Further reading and references

Barrow, G.M.(1979) Physical Chemistry. McGraw-Hill International. Pp. 531-534. ISBN 0-07-066170-7

Babarinde, A. (2009) Introduction to Quantum Chemistry. Lucky Odoni Publishers, Ijebu-Ode, ISBN 978-178-212-9

Porlie, N. Modern University Chemistry

Module 1: Atomic and molecular structures

Unit 5: Heat capacities of solids

Contents

Introduction 72

2.0 Objectives.. 73

Definition of heat capacity... 73

    3.1 Heat capacity of compressible bodies 74

    3.2 Relation between specific heats... 76

    3.3 Specific heat capacity... 77

    3.4 Dimensionless heat capacity 80

3.5 Solid phase 81

3.6 A Classical approach to heat capacity 82

3.7 A Quantum mechanical derivation of heat capacity 85

3.8 The Heat capacity function for low temperatures 86

Limit Using l'Hospital's rule 88

3.9 Heat capacity at absolute zero 89

4.0 Conclusion 90

5.0 Summary 90

6.0 Tutor marked assignment 91

7.0 Further reading and references 91

1.0 Introduction

Heat capacity is the measure of the heat energy required to increase the temperature of an object by a certain temperature interval. Heat capacity is an **extensive property** because its value is proportional to the amount of material in the object; for example, a bathtub of water has a greater heat capacity than a cup of water. Heat capacity is usually expressed in units of J/K (or J K^{-1}). For instance, one could write that the gasoline in a **55-gallon drum** has an average heat capacity of 347 kJ/K.

2.0 Objectives

By the end of this unit, you should be able to;

(a) define heat capacity;

(b) derive the relation between specific heats and

(c) derive the heat Capacity function for low temperatures.

3.0 Definition of heat capacity

The heat capacity of a substance, C, is the increase in internal energy of a substance U per unit increase in temperature T:

$$C = (\partial U/\partial T)$$

Heat capacity is mathematically defined as the ratio of a small amount of heat δQ added to the body, to the corresponding small increase in its temperature dT:

$$C = \left(\frac{\delta Q}{dT}\right)_{cond.} = T\left(\frac{dS}{dT}\right)_{cond.}$$

For thermodynamic systems with more than one physical dimension, the above definition does not give a single, unique quantity unless a particular infinitesimal path through the system's phase space has been defined (this means that one needs to know at all times where all parts of the system are, how much mass they have, and how fast they are moving). This information is used to account for different ways that heat can be stored as kinetic energy (energy of motion) and potential energy (energy stored in force fields), as an object expands or contracts. For all real systems, the path through these changes must be explicitly defined, since the value of heat capacity depends on which path from one temperature to another, is chosen. Of particular usefulness in this context are the values of heat capacity for constant volume, C_V, and constant pressure, C_P. These will be defined below.

3.1 Heat capacity of compressible bodies

The state of a simple compressible body with fixed mass is described by two thermodynamic parameters such as temperature T and pressure p. Therefore as mentioned above, one may distinguish between *heat capacity at constant volume*, C_V, and *heat capacity at constant pressure*, C_p:

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_p = \left(\frac{\delta Q}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

where

δQ is the infinitesimal amount of heat added,

dT is the subsequent rise in temperature.

The increment of internal energy is the heat added and the work added:

$$dU = T\,dS - p\,dV$$

So the heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The enthalpy is defined by $H = U + PV$. The increment of enthalpy is

$$dH = dU + (pdV + V\,dp)$$

which, after replacing dU with the equation above and cancelling the PdV terms reduces to:

$$dH = T\,dS + V\,dp.$$

So the heat capacity at constant pressure is

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p.$$

Note that this last “definition” is a bit circular, since the concept of “enthalpy” itself was *invented* to be a measure of heat absorbed or produced at constant pressures (the conditions in which chemists usually work). As such, enthalpy merely accounts for the extra heat which is produced or absorbed by pressure-volume work at constant pressure. Thus, it is not surprising that constant-pressure heat capacities may be defined in terms of enthalpy, since “enthalpy” was defined in the first place to make this so.

Analogous expressions for specific heat capacities at constant volume and at constant pressure are:

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

where *u* = specific internal energy and *h* = specific enthalpy. These intensive quantities can be expressed on a per mole basis or on a per mass basis, as long as consistency is maintained throughout the equation.

3.2 Relation between specific heats

Measuring the heat capacity at constant volume can be prohibitively difficult for liquids and solids. That is, small temperature changes typically require large pressures to maintain a liquid or solid at constant volume implying the containing vessel must be nearly rigid or at least very strong. Instead it is easier to measure the heat capacity at constant pressure (allowing the material to expand or contract as it wishes) and solve for the heat capacity at constant volume using mathematical relationships derived from the basic thermodynamic laws. Starting from the fundamental Thermodynamic relation one can show,

$$c_p - c_v = \frac{\alpha^2 T}{\rho \beta_T}$$

where,

α is the coefficient of thermal expansion,

β_T is the isothermal compressibility, and

ρ is density.

For an ideal gas, if ρ is expressed as molar density in the above equation, this equation reduces simply to Mayer's relation,

$$C_{p,m} - C_{v,m} = R$$

Where $C_{p,m}$ and $C_{v,m}$ are intensive property heat capacities expressed on a per mole basis at constant pressure and constant volume, respectively.

3.3 Specific heat capacity

The specific heat capacity of a material on a per mass basis is

$$c = \frac{\partial C}{\partial m},$$

which in the absence of phase transitions is equivalent to

$$c = E_m = \frac{C}{m} = \frac{C}{\rho V},$$

where

C is the heat capacity of a body made of the material in question,

m is the mass of the body,

V is the volume of the body, and

$$\rho = \frac{m}{V}$$

is the density of the material.

For gases, and also for other materials under high pressures, there is need to distinguish between different boundary conditions for the processes under consideration (since values differ significantly between different conditions). Typical processes for which a heat capacity may be defined include isobaric (constant pressure, $dp = 0$) or isochoric (constant volume, $dV = 0$) processes. The corresponding specific heat capacities are expressed as

$$c_p = \left(\frac{\partial C}{\partial m}\right)_p,$$

$$c_V = \left(\frac{\partial C}{\partial m}\right)_V.$$

A related parameter to c is Cv^{-1}, the volumetric heat capacity. In engineering practice, Cv for solids or liquids often signifies a volumetric heat capacity, rather than a constant-volume one. In such cases, the mass-specific heat capacity (specific heat) is often explicitly written with the subscript m, as Cm. Of course, from the above relationships, for solids one writes

$$c_m = \frac{C}{m} = \frac{c_V}{\rho}.$$

For pure homogeneous chemical compounds with established molecular or molar mass or a molar quantity is established, heat capacity as an intensive property can be expressed on a per mole basis instead of a per mass basis by the following equations analogous to the per mass equations:

$C_{p,m} = \left(\frac{\partial C}{\partial n}\right)_p$ = molar heat capacity at constant pressure

$$C_{V,m} = \left(\frac{\partial C}{\partial n}\right)_V$$ = molar heat capacity at constant volume

where n = number of moles in the body or thermodynamic system. One may refer to such a "per mole" quantity as *molar heat capacity* to distinguish it from specific heat capacity on a per mass basis.

3.4 Dimensionless heat capacity

The dimensionless *heat capacity* of a material is

$$C^* = \frac{C}{nR} = \frac{C}{Nk}$$

where

C is the heat capacity of a body made of the material in question (J/K)

n is the amount of matter in the body (mol)

R is the gas constant (J/(K·mol)

N is the number of molecules in the body. (dimensionless)

k is Boltzmann's constant (J/(K·molecule)

3.5 Solid phase

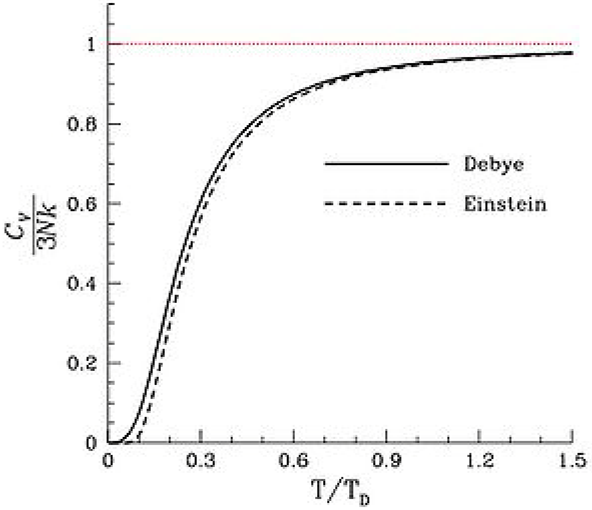


Figure 3.5.1: The dimensionless heat capacity divided by three, as a function of temperature as predicted by the Debye model and by Einstein's earlier model.

Source: "http://en.wikipedia.org/wiki/ "

The horizontal axis is the temperature divided by the Debye temperature. Note that, as expected, the dimensionless heat capacity is zero at absolute zero, and rises to a value of three as the temperature becomes much larger than the Debye temperature. The horizontal line above the plots corresponds to the classical limit of the Dulong-Petit law

For matter in a crystalline solid phase, the Dulong-Petit law, which was discovered empirically, states that the mole-specific heat capacity assumes the value 3 R. Indeed, for solid metallic chemical elements at room temperature, molar heat capacities range from about 2.8 R to 3.4 R (beryllium being a notable exception at 2.0 R).

The theoretical maximum heat capacity for larger multi-atomic gases at higher temperatures also approaches the Dulong-Petit limit of 3 R, so long as this is calculated per mole of atoms, not molecules. The reason is that gases with very large molecules, in theory have almost the same high-temperature heat capacity as solids, lacking only the (small) heat capacity contribution that comes from potential energy that cannot be stored between separate molecules in a gas. The Dulong-Petit "limit" results from the equipartition theorem, and as such is only valid in the classical limit of a microstate continuum, which is a high temperature limit. For light and non-metallic elements, as well as most of the common molecular solids based on carbon compounds at standard ambient temperature, quantum effects may also play an important role, as they do in multi-atomic gases. These effects usually combine to give heat capacities lower than 3 R per mole of *atoms* in the solid, although heat capacities calculated *per mole of molecules* in molecular solids may be more than 3 R. For example, the heat capacity of water ice at the melting point is about 4.6 R per mole of molecules, but only 1.5 R per mole of atoms. The lower number results from the "freezing out" of possible vibration modes for light atoms at suitably low temperatures, just as in many gases. These effects are seen in solids more often than liquids: for example the heat capacity of liquid water is again close to the theoretical 3 R per mole of atoms of the Dulong-Petit theoretical maximum.

For a more modern and precise analysis of the heat capacities of solids, especially at low temperatures, it is useful to use the idea of phonons.

3.6 A Classical approach to heat capacity

A good deal of insight may be obtained from a very simple model of a solid. Consider the solid to be a three dimensional lattice of atoms in which the atoms are held near equilibrium positions by forces. If the force on an atom is proportional to its deviation from its equilibrium position then it is called a harmonic oscillator. For zero deviation the force is zero so the force for small deviations is proportional to the deviation. Thus any such solid can be considered to be composed of harmonic oscillators. In a cubic lattice the atoms can oscillate in three directions.

The average energy E of a harmonic oscillator in one dimension is kT, where k is Boltzmann's constant. In three dimensions the average energy is 3kT. If there are N atoms in the lattice then the internal energy is U= N(3kT). Let A be Avogadro's number (6.025×10^{23}). Then dividing and multiplying the equation of U by A gives

$U = (N/A)(3AkT)$

The ratio (N/A) is the number of moles of the substance, n, and Ak is denoted as R. Thus

$U = n(3RT)$

so

$U_M = (U/n) = 3RT$

The heat capacity per unit mole of a substance at constant pressure is then defined as

$C_p = (\partial U_M/\partial T)$

and thus from the above

$C_p = 3R$

The value for C_p of 3R is about 6 calories per degree Kelvin. This is known as the Dulong and Petit value. It is a good approximation for the measured values for solids at room temperatures (300°K). At low temperatures the Dulong and Petit value is not a good approximation. Below is shown the heat capacity of metallic silver as a function of temperature.

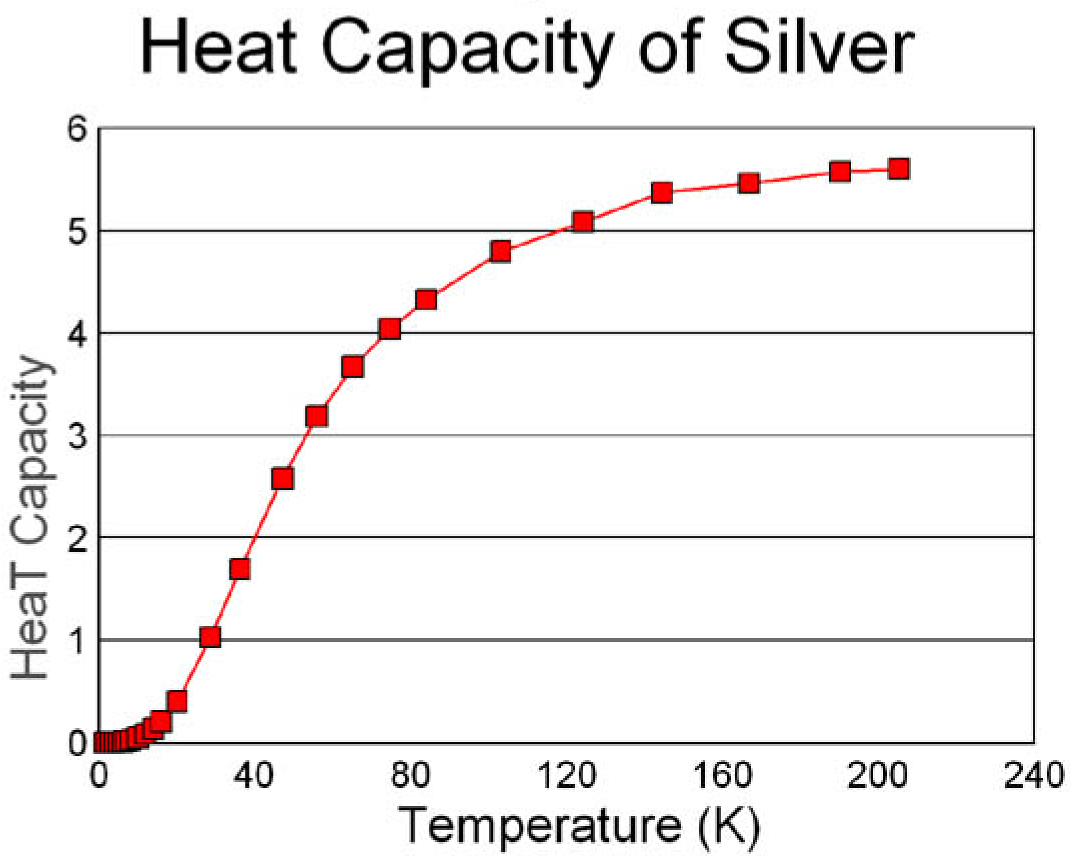


Figure 3.5.2: Heat capacity for silver at different temperatures.

Source: applet-magic.com *Thayer Watkins* Silicon Valley & Tornado Alley, USA

The shape of the curve for T near zero is of interest. It appears to be proportional to a power of T, say T^2 or T^3.

3.7 A Quantum mechanical derivation of heat capacity

According to Planck's law for the distribution of energy for an ensemble (collection) of harmonic oscillators the average energy E is given by

$$E = \hbar\omega/[\exp(\hbar\omega/kT) - 1]$$

where ħ is Planck's constant h divided by 2*pi; and ω is the characteristic frequency (circular) of the oscillators. This frequency is in the nature of a parameter for the substance and has to be determined empirically.

For temperature such that kT is much larger than $\hbar\omega$ the denominator becomes approximately $\hbar\omega/kT$ so E is approximately kT.

In general however

$U = NE = N3\hbar\omega/[\exp(\hbar\omega/kT) - 1]$

$U_M = 3A\hbar\omega/[\exp(\hbar\omega/kT) - 1]$

and hence

$C_p = -3A\hbar\omega/[\exp(\hbar\omega/kT) - 1]^2[\exp(\hbar\omega/kT)](-\hbar\omega/kT^2)$

With a little rearrangement this can be put into the form

$C_p = 3R(\hbar\omega/kT)^2\exp(\hbar\omega/kT)/[\exp(\hbar\omega/kT) - 1]^2$

Now if the numerator and denominator are divided by $[\exp(\hbar\omega/kT)]^2$ the result is

$C_p = 3R(\hbar\omega/kT)^2\exp(-\hbar\omega/kT)/[1 - \exp(-\hbar\omega/kT)]^2$

The attempt to obtain the limit of this expression as T→0 produces the ambiguous result of ∞/∞. The application of l'Hospital's Rule **two times** finally produces the result that the limit of C_p is zero as T→0.

3.8 The Heat capacity function for low temperatures

As mentioned above 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.

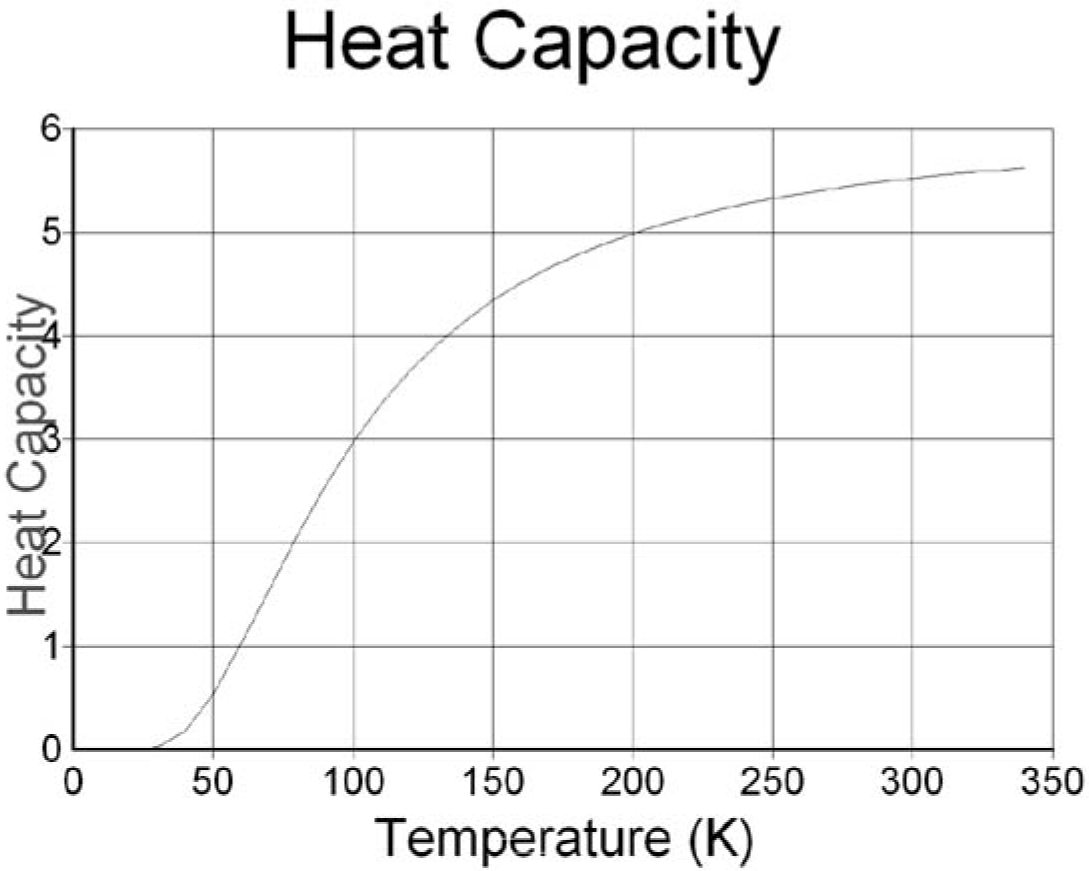


Figure 3.5.3: Heat capacity for solids at different temperatures.

Source: applet-magic.com *Thayer Watkins* Silicon Valley & Tornado Alley, USA

To investigate the behavior of the heat capacity function for small T it simplify matters let ħω/k, which has the dimensions of temperature, be denoted as θ. This parameter is sometimes called the Einstein temperature because it was Einstein who first formulated this line of analysis. (Einstein was far more adept at realizing the implications of the quantization of energy found by Planck than Planck himself.)

The heat capacity function is then:

$C_p = 3R(\theta/T)^2\exp(-\theta/T)/[1 - \exp(-\theta/T)]^2$

Matters can be made even simpler by replacing θ/T with z. Then

$C_p = 3Rz^2\exp(-z)/[1 - \exp(-z)]^2$

and

$\ln(C_p) = \ln(3R) + 2\ln(z) - z - 2\ln[1 - \exp(-z)]$

This means that $\ln(C_p)\to-\infty$ as $z\to+\infty$; i.e., $C_p\to0$ as $T\to0$.

(To be continued.)

Limit Using l'Hospital's Rule

$C_p = 3R(\hbar\omega/kT)^2\exp(-\hbar\omega/kT)/[1 - \exp(-\hbar\omega/kT)]^2$

The term $[1 - \exp(-\hbar\omega/kT)]^2$ approaches the limit of 1 as T→0 so let us ignore that term. Thus

$C_p = 3R(\hbar\omega/kT)^2/\exp(\hbar\omega/kT)$

and to simplify matters let ħω/k,

which has the dimensions of temperature,

be denoted as θ. Then

$C_p = 3R(\theta/T)^2/\exp(\theta/T)$

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

$3R(2(\theta^2)(-1/T^3)/(\exp(\theta/T)(-\theta/T^2) = 6R\theta(1/T)/\exp(\theta/T)$

which, as T→0, goes to ∞/∞

Thus l'Hospital's rule must be applied again, which gives

$6R\theta(-1/T^2)/(\exp(\theta/T)(\theta/T^2) = 6R/\exp(\theta/T)$

which has a limit of zero as T→0.

Thus $C_p \rightarrow 0$ as T→0.

3.9 Heat capacity at absolute zero

From the definition of entropy

$$TdS = \delta Q$$

we can calculate the absolute entropy by integrating from zero kelvin temperature to the final temperature T_f

$$S(T_f) = \int_{T=0}^{T_f} \frac{\delta Q}{T} = \int_0^{T_f} \frac{\delta Q}{dT}\frac{dT}{T} = \int_0^{T_f} C(T)\,\frac{dT}{T}.$$

The heat capacity must be zero at zero temperature in order for the above integral not to yield infinite absolute entropy, thus violating the third law of thermodynamics. One of the strengths of the Debye model is that (unlike the preceding Einstein model) it predicts the proper mathematical form of the approach of heat capacity toward zero, as absolute zero temperature is approached.

Activity A

1. write the mathematical expression for heat capacity.
2. show the relationship between heat capacity and specific heat capacity.

4.0 Conclusion

The heat capacity of a substance, C, is the increase in internal energy of a substance U per unit increase in temperature.

5.0 Summary

In this unit, we have learnt that:

- **(i)** heat capacity is an extensive property because its value is proportional to the amount of material in the object.
- **(ii)** the state of a simple compressible body with fixed mass is described by two thermodynamic parameters such as temperature T and pressure p.
- **(iii)** for pure homogeneous chemical compounds with established molecular or molar mass or a molar quantity is established, heat capacity as an intensive property can be expressed on a per mole basis instead of a per mass basis.

6.0 Tutor marked assignment

1. derive the expression for heat capacity at constant volume, C_V, and heat capacity at constant pressure, C_p.

2. derive the relationship between C_p and C_v.

7.0 Further reading and references

^ Laider, Keith, J. (1993). *The World of Physical Chemistry*. Oxford University Press. ISBN 0-19-855919-4.

^ Specific Heat.

^ P. Fraundorf (2003) Heat capacity in bits, *American Journal of Physics* **71**:11, 1142-1151. (arXiv:cond-mat/9711074)

^ The comparison must be made under constant-volume conditions — C_vH — so that no work is performed. Nitrogen's C_vH (100 kPa, 20 °C) = 20.8 J mol^{-1} K^{-1} vs. the monatomic gases which equal 12.4717 J mol^{-1} K^{-1}. Citations: W.H. Freeman's *Physical Chemistry*, Part 3: Change (422 kB PDF, here), Exercise 21.20b, Pg. 787. Also Georgia State University's *Molar Specific Heats of Gases*.

^ C. Michael Hogan, (1969) *Density of States of an Insulating Ferromagnetic Alloy* Phys. Rev. 188, 870 - 874, [Issue 2 – December 1969

^ IUPAC.org, Gold Book, *Standard Pressure*

^ Page 183 in: Medical biophysics. Flemming Cornelius. 6th Edition, 2008. (also giving a density of 1.06 kg/l)

^ *a b c d e f g* Table of Specific Heats

^ *a b c* Textbook: Young and Geller College Physics, 8e, Pearson Education, 2008

^ *a b* R.J. Crawford, Rotational molding of plastics

^ Faber P., Garby L., Fat content affects heat capacity: a study in mice. Acta Physiol Scand 1995;153:187-5.

"http://en.wikipedia.org/wiki/Specific_heat_capacity"

Module 2: Theory of chemical bonding

Unit 1: The Valence bond theory

Contents

1.0 Introduction 94

2.0 Objectives 95

(b) Define Hybridization of atomic orbitals; 95

3.0 Definition of valence bond theory 95

3.1 Hybridization of atomic orbitals 96

3.2 The sp hybrid atomic orbitals 97

3.3 The sp^2 hybrid orbitals 99

3.4 The sp^3 hybrid orbitals 100

3.5 The dsp^3 hybrid orbitals 101

3.6 The d^2sp^3 hybrid orbitals 102

3.7 Molecular shapes of compounds 103

3.8 The Centre atom 105

Activity A.. 107
3.9 Valence bond theory today 107
3.10 Applications of Valence bond theory 109
4.0 Conclusion 110
5.0 Summary 110
6.0 Tutor marked assignment 111
7.0 Further reading and other resources 111

1.0 Introduction

In chemistry, **valence bond theory** is one of two basic theories, along with molecular orbital theory, that were developed to use the methods of quantum mechanics to explain chemical bonding(Wikipedia, 2009). It focuses on how the atomic orbitals of the dissociated atoms combine on molecular formation to give individual chemical bonds. In contrast, molecular orbital theory has orbitals that cover the whole molecule. In 1916, G.N. Lewis proposed that a chemical bond forms by the interaction of two shared bonding electrons, with the representation of molecules as Lewis structures. In 1927 the Heitler-London theory was formulated which for the first time enabled the calculation of bonding properties of the hydrogen molecule H_2 based on quantum mechanical considerations. Specifically, Walter Heitler determined how to use Schrödinger's wave equation (1925) to show how two hydrogen atom join together, with plus, minus, and exchange terms, to form a covalent bond.

2.0 Objectives

By the end of this unit, you should be able to:

(a) define what valence bond theory is;

(b) define Hybridization of atomic orbitals; and

(c) explain how a chemical bond is formed.

3.0 Definition of valence bond theory

The **valence-bond approach** considers the overlap of the atomic orbitals (AO) of the participation atoms to form a chemical bond. Due to the overlapping, electrons are localized in the bond region. The overlapping AOs can be of different types, for example, a sigma bond may be formed by the overlapping the following AOs (Waterloo, 2009).

Chemical bonds formed due to overlap of atomic orbitals					
s-s	***s-p***	***s-d***	***p-p***	***p-d***	***d-d***
H-H **Li-H**	**H-C** **H-N** **H-F**	**H-Pd in palladium hydride**	**C-C** **P-P** **S-S**	**F-S in SF_6**	**Fe-Fe**

However, the atomic orbitals for bonding may not be "pure" atomic orbitals directly from the solution of the Schrodinger Equation. Often, the bonding atomic orbitals have a character of several possible types of orbitals. The methods to get an AO with the proper character for the bonding are called **hybridization**. The resulting atomic orbitals are called **hybridized atomic orbitals** or simply **hybrid orbitals**.

We shall look at the shapes of some hybrid orbitals first, because these shapes determine the shapes of the molecules.

3.1 Hybridization of atomic orbitals

The solution to the Schrodinger Equation provides the wavefunctions for the following atomic orbitals:

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, 4*s*, 4*p*, 4*d*, 4*f*, etc.

For atoms containing two or more electrons, the energy levels are shifted with respect to those of the H atom. An atomic orbital is really the energy state of an electron bound to an atomic nucleus. The energy state changes when one atom is bonded to another atom.

Quantum mechanical approaches by combining the wave functions to give new wavefunctions are called **hybridization** of atomic orbitals. Hybridization has a sound mathematical fundation, but it is a little too complicated to show the details here. Leaving out the jargons, we can say that an imaginary mixing process converts a set of atomic orbitals to a new set of **hybrid atomic orbitals** or **hybrid orbitals**.

At this level, we consider the following hybrid orbitals:

sp
sp^2
sp^3
sp^3d
sp^3d^2

3.2 The sp hybrid atomic orbitals

The ***sp* hybrid atomic orbitals** are possible states of electron in an atom, especially when it is bonded to others. These electron states have half 2*s* and half 2*p* characters. From a mathematical view point, there are two ways to combine the 2*s* and 2*p* atomic orbitals:

$sp_1 = 2s + 2p$
$sp_2 = 2s - 2p$

These energy states (sp_1 and sp_2) have a region of high electron probability each, and the two atomic orbitals are located opposite to each other, centered on the atom. The sp hybrid orbitals are represented by this photograph.

For example, the molecule H-Be-H is formed due to the overlapping of two 1*s* orbitals of 2 H atoms and the two *sp* hybridized orbitals of Be. Thus, the H-Be-H molecule is linear. The diagram here shows the overlapping of AOs in the molecule H-Be-H.

1*s* 1*s*
H-Be-H H sp^1 Be sp^2 H
1*s* 1*s*

The ground state electronic configuration of Be is $1s^22s^2$, and one may think of the electronic configuration "before" bonding as $1s^2sp^2$. The two electrons in the *sp* hybrid orbitals have the same energy.

You may say that the concept of hybridizing AOs for the bonding is just a story made up to explain the molecular shape of Cl-Be-Cl. You are right! The story is lovely and interesting, though.

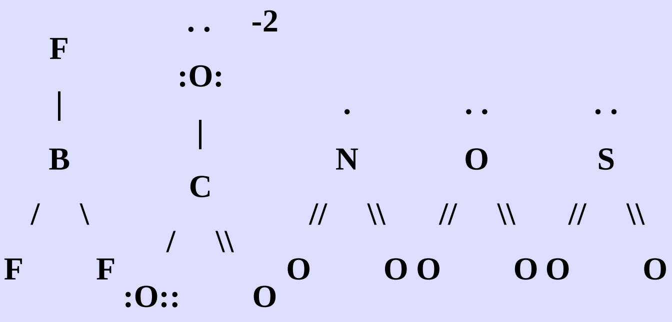
In general, when two and only two atoms bond to a third atom and the third atom makes use of the *sp* hybridized orbitals, the three atoms are on a straight line. For example, *sp* hybrid orbitals are used in the central atoms in the molecules shown on the right.

Linear molecules
ClBeCl
HCCH
HCN
O=C=O

3.3 The sp^2 hybrid orbitals

The energy states of the valence electrons in atoms of the second period are in the 2*s* and 2*p* orbitals. If we mix two of the 2*p* orbitals with a 2*s* orbital, we end up with **three *sp*^{2} hybridized orbitals**. These three orbitals lie on a plane, and they point to the vertices of a equilateral triangle. When the central atom makes use of *sp*^{2} hybridized orbitals, the compound so formed has a trigonal shape. BF_3 is such a molecule:

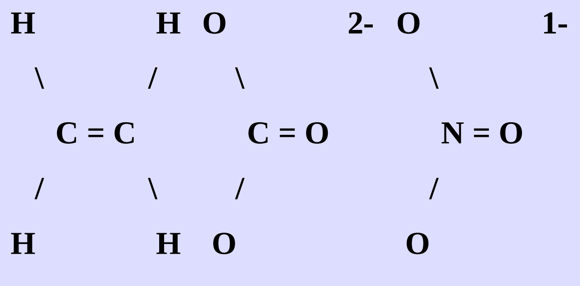
Molecules with *sp*^{2} Hybrid orbitals



Not all three *sp*^{2} hybridized orbitals have to be used in bonding. One of the orbitals may be occupied by a pair or a single electron. If we do not count the unshared electrons, these molecules are bent, rather than linear. The three molecules shown together with the BF_3 molecule are such molecules (Waterloo, 2009).

Carbon atoms also makes use of the *sp*^{2} hybrid orbitals in the compound $H_2C{=}CH_2$. In this molecule, the remaining *p* orbital from each of the carbon overlap to form the additional pi, □, bond.

Planar molecules with *sp*^{2} Hybrid orbitals



Other ions such as CO_3^{2-}, and NO_3^-, can also be explained in the same way.

3.4 The sp^3 hybrid orbitals

Mixing one *s* and all three *p* atomic orbitals produces a set of four equivalent *sp*^{3} hybrid atomic orbitals. The four *sp*^{3} hybrid orbitals points towards the vertices of a tetrahedron. When *sp*^{3} hybrid orbitals are used for the central atom in the formation of molecule, the molecule is said to have the shape of a tetrahedron. The typical molecule is CH_4, in which the 1*s* orbital of an H atom overlap with one of the *sp*^{3} hybrid orbitals to form a C-H bond. Four H atoms form four such bonds, and they are all equivalent. The CH_4 molecule is the most cited molecule to have a tetrahedral shape. Other molecules and ions having tetrahedral shapes are SiO_4^{4-}, SO_4^{2-},

As are the cases with sp^2, hybrid orbitals, one or two of the sp^3 hybrid orbitals may be occupied by non-bonding electrons (Waterloo, 2009). Water and ammonia are such molecules.

Tetrahedral arrangements of CH_4, NH_3E and OH_2E_2

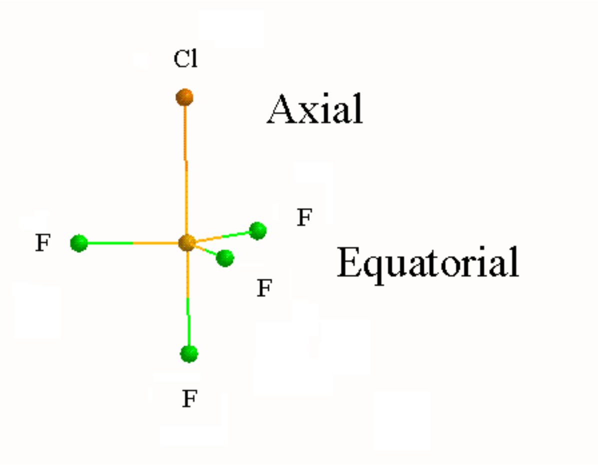
```
H      H H      H H      H
 \    /   \    /   \    /
    C        N        O
   / \      / \      / \
  H  H     :  H     :  :
```

The C, N and O atoms in CH_4, NH_3, OH_2 (or H_2O) molecules use the sp^3 hybrid orbitals, however, a lone pair occupies one of the orbitals in NH_3, and two lone pairs occupy two of the sp^3 hybrid orbitals in OH_2. The lone pairs must be considered in the VSEPR model, and we can represent a lone pair by E, and two lone pairs by E_2. Thus, we have NH_3E and OH_2E_2 respectively.

The *VSEPR number* is equal to the number of bonds plus the number of lone pair electrons. Does not matter what is the order of the bond, any bonded pair is considered on bond. Thus, the *VSEPR number* is 4 for all of CH_4, $:NH_3$, $::OH_2$.

According the VSEPR theory, the lone electron pairs require more space, and the H-O-H angle is 105 degrees, less than the ideal tetrahedral angle of 109.5 degrees.

3.5 The dsp^3 hybrid orbitals



The five *dsp*^{3} hybrid orbitals resulted when one 3*d*, one 3*s*, and three 3*p* atomic orbitals are mixed. When an atom makes use of fice *dsp*^{3} hybrid orbitals to bond to five other atoms, the geometry of the molecule is often a **trigonalbipyramidal**. For example, the molecule $PClF_4$ displayed here forms such a structure. In this diagram, the Cl atom takes up an axial position of the trigonalbipyramid. There are structures in which the Cl atom may take up the equatorial position. The change in arrangement is accomplished by simply change the bond angles. This link discusses this type of configuration changes of this molecule.

Some of the *dsp*^{3} hybrid orbitals may be occupied by electron pairs. The shapes of these molecules are interesting. In $TeCl_4$, only one of the hybrid *dsp*^{3} orbitals is occupied by a lone pair. This structure may be represented by $TeCl_4E$, where E represents a lone pair of electrons. Two lone pairs occupy two such orbitals in the molecule BrF_3, or BrF_3E_2. The compound SF_4 is another AX_4E type, and many interhalogen compounds ClF_3 and IF_3 are AX_3E_2 type. The ion I_3^- is of the type AX_2E_3.

3.6 The d^{2}sp^3 hybrid orbitals

The six *d*^{2}*sp*^{3} hybrid orbitals resulted when two 3*d*, one 3*s*, and three 3*p* atomic orbitals are mixed. When an atom makes use of six *d*^{2}*sp*^{3} hybrid orbitals to bond to six other atoms, the molecule takes the shape of an octahedron, in terms of molecular geometry. The gas compound SF_6 is a typical such structure. This link provides other shapes as well. There are also cases that some of the *d*^{2}*sp*^{3} hybrid orbitals are occupied by lone pair electrons leading to the structures of the following types:

AX_6, AX_5E, AX_4E_2 AX_3E_3 and AX_2E_4
IOF_5, IF_5E, XeF_4E_2

No known compounds of AX_3E_3 and AX_2E_4 are known or recognized, because they are predicted to have a T shape and linear shape respectively when the lone pairs of electrons are ignored (Waterloo, 2009).

Activity A

(a) define what valence bond theory is
(b) define Hybridization of atomic orbitals and
(c) explain how a chemical bond is formed.

3.7 Molecular shapes of compounds

While the hybridized orbitals were introduced, in the foregoing discussion, Valence-shell electron-pair repulsion (VSEPR) model was included to suggest the shapes of various molecules. Specifically, the VSEPR model counts unshared electron pairs and the bonded atoms as the *VSEPR number*. A single-, double- and tripple-bond is considered as 1. After having considered the hybridized orbitals and the VSEPR model, we can not take a systematic approach to rationalize the shapes of many molecules based on the number of valence electrons.

A summary in the form of a table is given here to account for the concepts of **hybrid orbitals, valence bond theory, VSEPR, resonance structures**, and **octet rule**. In this table, the geometric shapes of the molecules are described by **linear, trigonal planar, tetrahedral, trigonal bypyramidal, and octahedral**. The hybrid orbitals uses are sp, sp^2, sp^3, dsp^3, and d^2sp^3. The *VSEPR number* is the same for all molecules of each group. Instead of using NH_3E, and OH_2E_2, we use $:NH_3$, $::OH_2$ to emphasize the unshared (or lone) electron pairs.

Table 2.1.1: A summary of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule.

Linear	**Trigonal planar**	**Tetrahedral**	**Trigonal bipyramidal**	**Octahedral**
sp	sp^2	sp^3	dsp^3	d^2sp^3
BeH_2	BH_3	CH_4	PF_5	SF_6
BeF_2	BF_3	CF_4	PCl_5	IOF_5
CO_2	CH_2O	CCl_4	$PFCl_4$	PF_6^-
HCN	**(>C=O)**	CH_3Cl	$:SF_4$	SiF_6^{2-}
HC☐CH	**>C=C<**	NH_4^+	$:TeF_4$	$:BrF_5$
	CO_3^{2-}	$:NH_3$	$::ClF_3$	$:IF_5$
	benzene	$:PF_3$	$::BrF_3$	$::XeF_4$
	graphite	$:SOF_2$	$:::XeF_2$	
	fullerenes	$::OH_2$	$:::I_3^-$	
	$\bullet NO_2$	$::SF_2$	$(:::I\ I_2^-)$	
	N_3^-		$:::ICl_2^-$	
	$:OO_2$ (O_3)	SiO_4^{4-}		
	$:SO_2$	PO_4^{3-}		
	SO_3	SO_4^{2-}		
		ClO_4^-		

• a lone odd electron **:** a lone electron pair

This table correlates a lot of interesting chemical concepts in order to understand the molecular structures of these compounds or ions. There are some intriguing chemical relationships among the molecules in each column for you to ponder (Waterloo, 2009).
Only Be and C atoms are involved in linear molecules. In gas phase, BeH_2 and BeF_2 are stable, and these molecules do not satisfy the octet rule. The element C makes use of *sp* hybridized orbitals and it has the ability to form double and triple bonds in these linear molecules.

Carbon compounds are present in trigonal planar and tetrahedral molecules, using different hybrid orbitals. The extra electron in nitrogen for its compounds in these groups appears as lone unpaired electron or lone electron pairs. More electrons in O and S lead to compounds with lone electron pairs. The five-atom anions are tetrahedral, and many resonance structures can be written for them (Waterloo, 2009).

Trigonal bipyramidal and octahedral molecules have 5 and 6 VSEPR pairs. When the central atoms contain more than 5 or 6 electrons, the extra electrons form lone pairs. The number of lone pairs can easily be derived using Lewis dot structures for the valence electrons.

In describing the shapes of these molecules, we often ignore the lone pairs. Thus, $\bullet NO_2$, N_3^-, $:OO_2$ (O_3), and $:SO_2$ are **bent molecules** whereas $:NH_3$, $:PF_3$, and $:SOF_2$ are pyramidal. You already know that $::OH_2$ (water) and $::SF_2$ are bent molecules.

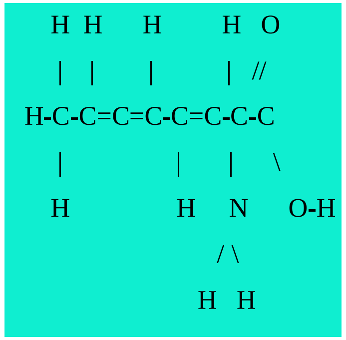
The lone electron pair takes up the equatorial location in $:SF_4$, which has the same structure as $:TeF_4$ described earlier. If you lay a model of this molecule on the side, it looks like a *butterfly*. By the same reason, $::ClF_3$ and $::BrF_3$ have a *T* shape, and $:::XeF_2$, $:::I_3^-$, and $:::ICl_2^-$ are linear.

Similarly, $:BrF_5$ and $:IF_5$ are square pyramidal whereas $::XeF_4$ is square planar.

3.8 The Centre atom

Usually, the atom in the centre is more electropositive than the terminal atoms. However, the H and halogen atoms are usually at the terminal positions because they form only one bond. Take a look at the chemical formulas in the table, and see if the above statement is true.

However, the application of VSEPR theory can be expanded to complicated molecules such as



By applying the VSEPR theory, one deduces the following results:

- H-C-C bond angle = 109°
- H-C=C bond angle = 120°, geometry around C trigonal planar
- C=C=C bond angle = 180°, in other words linear
- H-N-C bond angle = 109°, tetrahedral around N
- C-O-H bond angle = 105 or 109°, 2 lone electron pairs around O

Activity B

(a) Which atom in the formula is usually the centre atom?
(b) In terms of valence bond theory, how is a chemical bond formed?
(c) When one *s* and two *p* atomic orbitals are used to generate hybrid orbitals, how many hybrid orbitals will be generated?

3.9 Valence bond theory today

Valence bond theory now complements Molecular Orbital Theory (MO theory), which does not adhere to the VB idea that electron pairs are localized between two specific atoms in a molecule but that they are distributed in sets of molecular orbitals which can extend over the entire molecule. MO theory can predict magnetic properties in a straightforward manner, while valence bond theory gives similar results but is more complicated. Valence bond theory views aromatic properties of molecules as due to resonance between Kekule, Dewar and possibly ionic structures, while molecular orbital theory views it as delocalization of the π-electrons. The underlying mathematics is also more complicated limiting VB treatment to relatively small molecules. On the other hand, VB theory provides a much more accurate picture of the reorganization of electronic charge that takes place when bonds are broken and formed during the course of a chemical reaction. In particular, valence bond theory correctly predicts the dissociation of homonuclear diatomic molecules into separate atoms, while simple molecular orbital theory predicts dissociation into a mixture of atoms and ions.

More recently, several groups have developed what is often called modern valence bond theory. This replaces the overlapping atomic orbitals by overlapping valence bond orbitals that are expanded over a large number of basis functions, either centered each on one atom to give a classical valence bond picture, or centered on all atoms in the molecule. The resulting energies are more competitive with energies from calculations where electron correlation is introduced based on a Hartree-Fock reference wavefunction. The most recent text is by Shaik and Hiberty.

Modern valence bond theory is the term used to describe applications of valence bond theory with computer programs that are competitive in accuracy and economy with programs for the Hartree-Fock method and other molecular orbital based methods. The latter methods dominated quantum chemistry from the advent of digital computers because they were easier to program. The early popularity of valence bond methods thus declined. It is only recently that the programming of valence bond methods has improved. These developments are due to and described by Gerratt, Cooper, Karadakov and Raimondi (1997); Li and McWeeny (2002); Song, Mo, Zhang and Wu (2005); and Shaik and Hiberty (2004). In its simplest form the overlapping atomic orbitals are replaced by orbitals which are expanded as linear combinations of the atom-based basis functions. This expansion is optimized to give the lowest energy. This procedure gives good energies without including ionic structures.

For example, in the hydrogen molecule, classic valence bond theory uses two 1s atomic orbitals (a and b) on the two hydrogen atoms respectively and then constructs a covalent structure:-

$\Phi_C = ((a(1)b(2) + b(1)a(2)) ((\alpha(1)\beta(2) - \beta(1)\alpha(2))$

and then an ionic structure:-

$\Phi_I = ((a(1)a(2) + b(1)b(2)) ((\alpha(1)\beta(2) - \beta(1)\alpha(2))$

The final wave function is a linear combination of these two functions. Coulson and Fischer pointed out that a completely equivalent function is:-

$\Phi_{CF} = ((a+kb)(1)(b+ka)(2) + (b+ka)(1)(a+kb)(2)) ((\alpha(1)\beta(2) - \beta(1)\alpha(2))$

as expanding this out gives a linear combination of the covalent and ionic structures. Modern valence bond theory replaces the simple linear combination of the two atomic orbitals with a linear combination of all orbitals in a larger basis set. The two resulting valence bond orbitals look like an atomic orbital on one hydrogen atom slightly distorted towards the other hydrogen atom. Modern valence bond theory is thus an extension of the Coulson-Fischer method.

There are a large number of different valence bond methods. Most use n valence bond orbitals for n electrons. If a single set of these orbitals is combined with all linear independent combinations of the spin functions, we have spin-coupled valence bond theory. The total wave function is optimized using the variation principle by varying the coefficients of the basis functions in the valence bond orbitals and the coefficients of the different spin functions. In other cases only a sub-set of all possible spin functions is used. Many valence bond methods use several sets of the valence bond orbitals. Be informed that different authors use different names for these different valence bond methods.

3.10 Applications of Valence bond theory

An important aspect of the VB theory is the condition of maximum overlap which leads to the formation of the strongest possible bonds. This theory is used to explain the covalent bond formation in many molecules.

For Example in the case of F_2 molecule the F - F bond is formed by the overlap of p_z orbitals of the two F atoms each containing an unpaired electron. Since the nature of the overlapping orbitals are different in H_2 and F_2 molecules, the bond strength and bond lengths differ between H_2 and F_2 molecules.

In a HF molecule the covalent bond is formed by the overlap of 1s orbital of H and $2p_z$ orbital of F each containing an unpaired electron. Mutual sharing of electrons between H and F results in a covalent bond between HF.

4.0 Conclusion

Valence bond theory focuses on how the atomic orbitals of the dissociated atoms combine on molecular formation to give individual chemical bonds.

5.0 Summary

In this unit, we have learnt that:

(i) the valence-bond approach considers the overlap of the atomic orbitals (AO) of the participation atoms to form a chemical bond,

(ii) due to the overlapping, electrons are localized in the bond region,

(iii) the overlapping AOs can be of different types,

(iv) the methods to get an AO with the proper character for the bonding are called hybridization and

(v) the resulting atomic orbitals are called hybridized atomic orbitals or simply hybrid orbitals.

6.0 Tutor marked assignment

(i) In the structures of SO_2 and NO_2, what are the values of the bond angles?

(ii) What is the geometrical shape of the molecule CH_4, methane?

(iii) What do you expect the bond angles to be in the NH_4^+ ion?

(iv) What hybrid orbitals does the C atom use in the compound H-C☐CH, in which the molecule is linear?

(v) What is the shape of the molecule SF_6?

(vi) Phosphorus often forms a five coordinated compound PX_5. What hybrid orbitals does P use in these compounds?

7.0 Further reading and other resources

Coulson, C. A. and Fischer, I. (1949). Phil. Mag. vol 40, p. 386

Gerratt, J., Cooper, D. L., Karadakov, P. B. and Raimondi, M. (1997). "Modern Valence Bond Theory", *Chemical Society Reviews*, **26**, 87

Hargittai, I. (1995). When Resonance Made Waves, The Chemical Intelligencer 1, 34

Li, J. and McWeeny, R. (2002). "VB2000: Pushing Valence Bond Theory to new limits",*International Journal of Quantum Chemistry*, **89**, 208,.

Murrel, J. N.; S. F. Tedder (1985). *The Chemical Bond*. John Wiley & Sons. 0-471-90759-6. Retrieved August 2, 2009 from website:

http://en.wikipedia.org/wiki/special:Booksources

Shaik, S. and Hiberty, P. C. (2004)"Valence Bond theory, its History, Fundamentals and Applications. A Primer", *Reviews of Computational Chemistry*, **20**, 1. A recent review that covers, not only their own contributions, but the whole of modern valence bond theory.

Retrieved from "http://en.wikipedia.org/wiki/Modern_valence_bond_theory"

Shaik, Sason S.; Phillipe C. Hiberty (2008). *A Chemist's Guide to Valence Bond Theory*. New Jersey: Wiley-Interscience. 978-0-470-03735-5. Retrieved August 2, 2009 from website: http://en.wikipedia.org/wiki/special:Booksources

Song, L., Mo, Y., Zhang, Q. and Wu, W. (2005) "XMVB: A program for *ab initio* nonorthogonal valence bond computations", *Journal of Computational Chemistry*, **26**, 514.

Walter Heitler - Key participants in the development of Linus Pauling's *The Nature of the Chemical Bond*.

Retrieved August 2, 2009 from website: http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/people/heitler.html

Wikipedia Encyclopedia, Retrieved August 2, 2009 from website: http://en.wikipedia.org

Module 2: Theory of chemical bonding

Unit 2: The molecular orbital theory

Contents

1.0 Introduction 115

2.0 Objectives 116

3.0 Definition molecular orbital theory 117

  3.1 Overview 117

  3.2 Some properties of molecular orbital 118

  3.3 Examples on molecular orbital theory: 118

  3.4 Atomic and molecular Orbitals 121

  3.5 Orbitals for selected molecules 122

  3.6 Valence bond model versus molecular orbital theory 129

3.7 Using the molecular orbital model to explain why Some molecules do not exist 130
4.0 Conclusion 131
5.0 Summary 131
6.0 Tutor marked assignment 131
7.0 Further reading and other resources 132

1.0 Introduction

In atoms, electrons occupy atomic orbitals, but in molecules they occupy similar molecular orbitals which surround the molecule. The simplest molecule is hydrogen, which can be considered to be made up of two separate protons and electrons. There are two molecular orbitals for hydrogen; the lower energy orbital has its greater electron density between the two nuclei. This is the bonding molecular orbital - and is of lower energy than the two *1s* atomic orbitals of hydrogen atoms making this orbital more stable than two separated atomic hydrogen orbitals. The upper molecular orbital has a node in the electronic wave function and the electron density is low between the two positively charged nuclei. The energy of the upper orbital is greater than that of the *1s* atomic orbital, and such an orbital is called an antibonding molecular orbital (W. Locke and the ICSTM, 1996,1997).

Normally, the two electrons in hydrogen occupy the bonding molecular orbital, with anti-parallel spins. If molecular hydrogen is irradiated by ultra-violet (UV) light, the molecule may absorb the energy, and promote one electron into its antibonding orbital (σ^*), and the atoms will separate. The energy levels in a hydrogen molecule can be represented in a diagram - showing how the two 1s atomic orbitals combine to form two molecular orbitals, one bonding (σ) and one antibonding (σ^*). This is shown below - by clicking upon either the σ or σ^* molecular orbital in the diagram - it will show graphically in a window to the right:

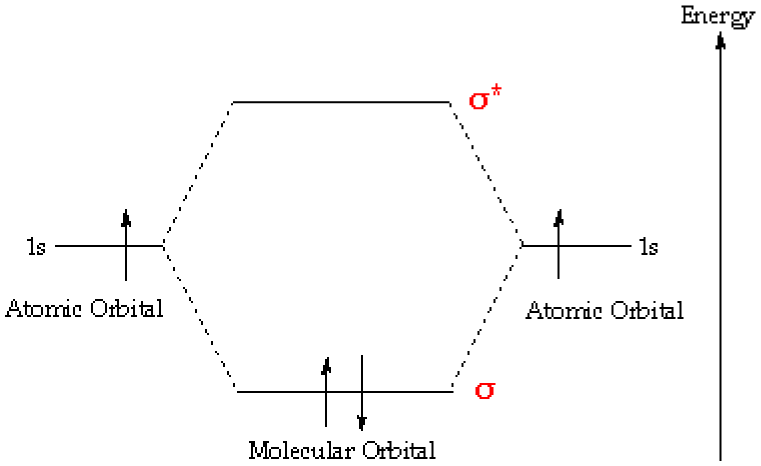


Figure 2.2.1: The energy levels in a hydrogen molecule. ***Source*:** W. Locke and the ICSTM Department of Chemistry.

2.0 Objectives

By the end of this unit, you should be able to:

(a) define what molecular orbital is;
(b) define what molecular orbital theory is;
(c) define properties of molecular orbital;
(d) define bonding molecular orbital
(e) define antibonding molecular orbital and

(f) illustrate pictorially molecular orbitals for several organic and inorganic molecules

3.0 Definition of molecular orbital theory

In chemistry, molecular orbital theory (*MO theory*) is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule (Wikipedia, 2009). In this theory, each molecule has a set of molecular orbitals, in which it is assumed that the molecular orbital wave function ψ_f may be written as a simple weighted sum of the n constituent atomic orbitals χ_i, according to the following equation:

$$\psi_j = \sum_{i=1}^{n} c_{ij}\chi_i$$

The c_{ij} coefficients may be determined numerically by substitution of this equation into the Schrödinger equation and application of the variational principle. This method is called the linear combination of atomic orbitals approximation and is used in computational chemistry. An additional unitary transformation can be applied on the system to accelerate the convergence in some computational schemes. Molecular orbital theory was seen as a competitor to valence bond theory in the 1930s, before it was realized that the two methods are closely related and that when extended they become equivalent.

3.1 Overview

Molecular orbital (MO) theory uses a linear combination of atomic orbitals to form molecular orbitals which cover the whole molecule. These are often divided into bonding orbitals, anti-bonding orbitals, and non-bonding orbitals. A molecular orbital is merely a Schrödinger orbital which includes several, but often only two nuclei.

3.2 Some properties of molecular orbital:

- The number of molecular orbitals is equal to the number the atomic orbitals included in the linear expansion,
- If the molecule has some symmetry, the degenerate atomic orbitals (with the same atomic energy) are grouped in linear combinations (called **symmetry adapted atomic orbitals (SO)**) which belong to the representation of the symmetry group, so the wave functions that describe the group are known as **symmetry-adapted linear combinations** (**SALC**).
- The number of molecular orbitals belonging to one group representation is equal to the number of symmetry adapted atomic orbitals belonging to this representation,
- Within a particular representation, the symmetry adapted atomic orbitals mix more if their atomic energy levels is closer.

3.3 Examples on molecular orbital theory:

H_2

H_2 1sσ* antibonding molecular orbital

As a simple example consider the hydrogen molecule, H_2 (see molecular orbital diagram), with the two atoms labelled H' and H". The lowest-energy atomic orbitals, 1s' and 1s", do not transform according to the symmetries of the molecule. However, the following symmetry

Adapted atomic orbitals do:

1s' - 1s"	Antisymmetric combination: negated by reflection, unchanged by other operations
1s' + 1s"	Symmetric combination: unchanged by all symmetry operations

The symmetric combination (called a bonding orbital) is lower in energy than the basis orbitals, and the antisymmetric combination (called an antibonding orbital) is higher. Because the H_2 molecule has two electrons, they can both go in the bonding orbital, making the system lower in energy (and hence more stable) than two free hydrogen atoms. This is called a covalent bond. The *bond order* is equal to the number of bonding electrons minus the number of antibonding electrons, divided by 2. In this example there are 2 electrons in the bonding orbital and none in the antibonding orbital; the bond order is 1, and there is a single bond between the two hydrogen atoms (Wikipedia, 2009).

He_2

On the other hand, consider the hypothetical molecule of He_2, the atoms labelled He' and He". Again, the lowest-energy atomic orbitals, 1s' and 1s", do not transform according to the symmetries of the molecule, while the following symmetry adapted atomic orbitals do:

1s' - 1s"	Antisymmetric combination: negated by reflection, unchanged by other operations
1s' + 1s"	Symmetric combination: unchanged by all symmetry operations

Similar to the molecule H_2, the symmetric combination (called a bonding orbital) is lower in energy than the basis orbitals, and the antisymmetric combination (called an antibonding orbital) is higher. However, in its neutral ground state, each Helium atom contains two electrons in its 1s orbital, combining for a total of four electrons. Two electrons fill the lower energy bonding orbital, while the remaining two fill the higher energy antibonding orbital. Thus, the resulting electron density around the molecule does not support the formation of a bond between the two atoms (called a sigma bond), and the molecule does therefore not exist. Another way of looking at it is that there are two bonding electrons and two antibonding electrons; therefore, the bond order is 0 and no bond exists (Wikipedia, 2009).

MO diagrams

For more complicated molecules, the wave mechanics approach loses utility in a qualitative understanding of bonding (although is still necessary for a quantitative approach). The qualitative approach of MO uses a molecular orbital diagram. In this type of diagram, the molecular orbitals are represented by horizontal lines; the higher a line, the higher the energy of the orbital, and degenerate orbitals are placed on the same level with a space between them. Then, the electrons to be placed in the molecular orbitals are slotted in one by one, keeping in mind the Pauli exclusion principle and Hund's rule of maximum multiplicity (only 2 electrons, having opposite spins, per orbital; have as many unpaired electrons on one energy level as possible before starting to pair them).

HOMO and LUMO

The highest occupied molecular orbital and lowest unoccupied molecular orbital are often referred to as the HOMO and LUMO, respectively. The difference of the energies of the HOMO and LUMO, termed the band gap, can sometimes serve as a measure of the excitability of the molecule: the smaller the energy, the more easily it will be excited.

3.4 Atomic and Molecular Orbitals

By sharing electron, molecules can form bonds, and it is possible to regard the sharing of two electrons by two atoms as constituting a chemical bond. Atoms can share one, two or three electrons (forming single, double and triple bonds).

A hydrogen atom consists of a nucleus (a *proton*) and an *electron*. It is not possible to accurately determine the position of the electron, but it is possible to calculate the probability of finding the electron at any point around the nucleus. With a hydrogen atom the probability distribution is spherical around the nucleus and it is possible to draw a spherical boundary surface, inside which there is a 95% possibility of finding the electron. The electron has a fixed energy and a fixed spatial distribution called an *orbital*. In the helium atom there are two electrons associated with the helium nucleus. The electrons have the same spatial distribution and energy (*ie*. they occupy the same orbital), but they differ in their spin (Pauli exlusion principle). In general: electrons in atomic nuclei occupy orbitals of fixed energy and spatial distribution, and each orbital only contains a maximum of two electrons with anti-parallel spins.

Activity A

- **a.** Define what molecular orbital
- **b.** Define molecular orbital theory

c. Define properties of molecular orbital

d. Define bonding molecular orbital

e. Define antibonding molecular orbital

3.5 Orbitals for selected molecules

This section illustrates pictorially molecular orbitals for several organic and inorganic molecules. If possible - the energy level diagram is included and clicking upon the relevant level will generate the accompanying molecular orbital in the right-hand frame (W. Locke and the ICSTM, 1996,1997).

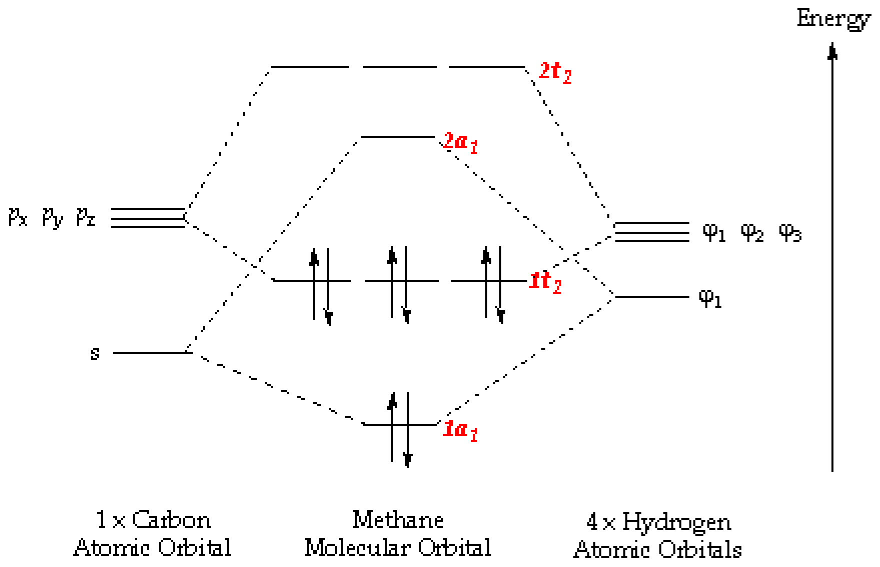


Figure 2.2.2:The energy levels in different molecules.

Source**:** W. Locke and the ICSTM Department of Chemistry.

Ethane:

The ethane molecule has fourteen valence electrons occupying seven bonding molecular orbitals. As can be seen from the energy diagram - four of the molecular orbitals occur as degenerate pairs. Like in methane - the molecular orbitals of ethane show increasing nodal structure with increasing orbital energy (W. Locke and the ICSTM, 1996, 1997).

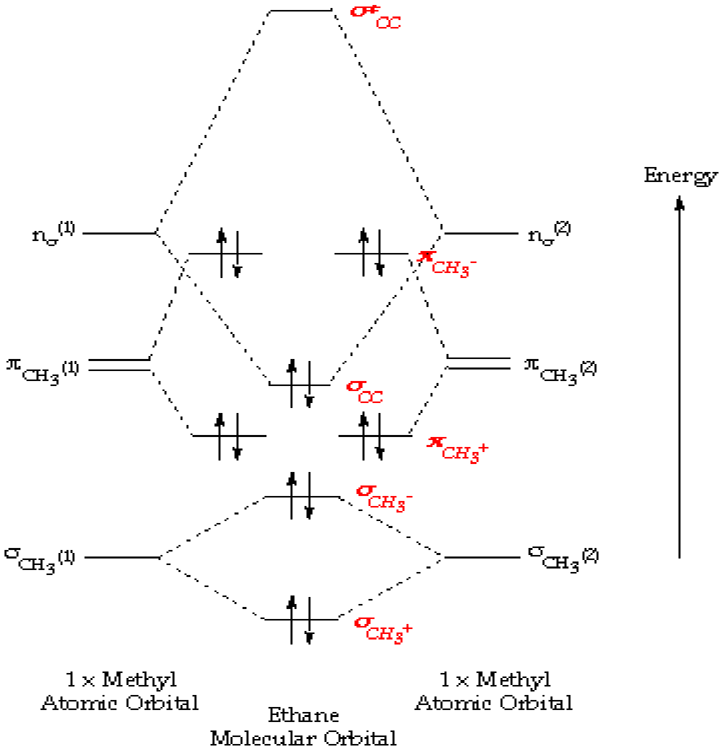


Figure 2.2.3: The molecular orbitals of ethane show increasing nodal structure with increasing orbital energy. *Source*: W. Locke and the ICSTM Department of Chemistry.

Molecules with double bonds

In molecules where the number of bonding electron pairs exceeds the number of unions between atoms, the extra electrons occupy higher energy molecular orbitals than the orbitals found in molecules where the number of bonding electron pairs equals the number of unions between atoms. These are double bonds, and the orbitals have a nodal plane containig the atoms sharing these π-type orbitals.

Ethene:

The simplest alkene is ethene. Its chemistry is dominated by two "*frontier orbitals*", that is the Highest Occupied Molecular Orbital (**HOMO**) and the Lowest Unoccupied Molecular Orbital (**LUMO**). For the ethene orbital energy diagram these are shown as π_{CC} for the HOMO, and π^{*}_{CC} for the LUMO.An important property of the ethene molecule, and alkenes in general is the existence of a high barrier to rotation about the **C=C** which tends to hold the molecule flat (W. Locke and the ICSTM, 1996,1997).For the energy diagram and pictorial view of the orbitals - please see below:

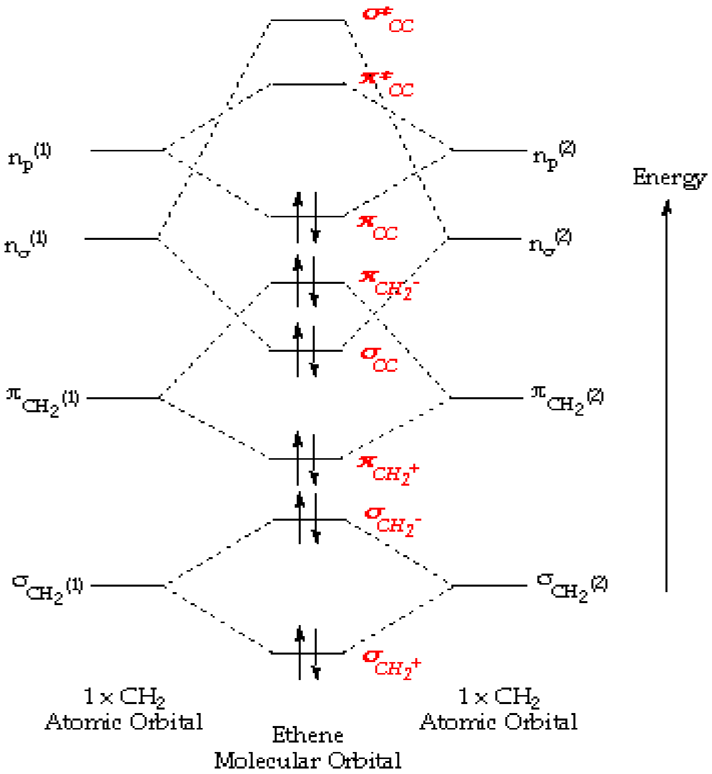


Figure 2.2.4: The molecular orbitals of ethene show increasing nodal structure with increasing orbital energy.*Source*: W. Locke and the ICSTM Department of Chemistry.

Molecules with triple bond

Ethyne:

For the energy diagram and pictorial view of the orbitals - please see below:

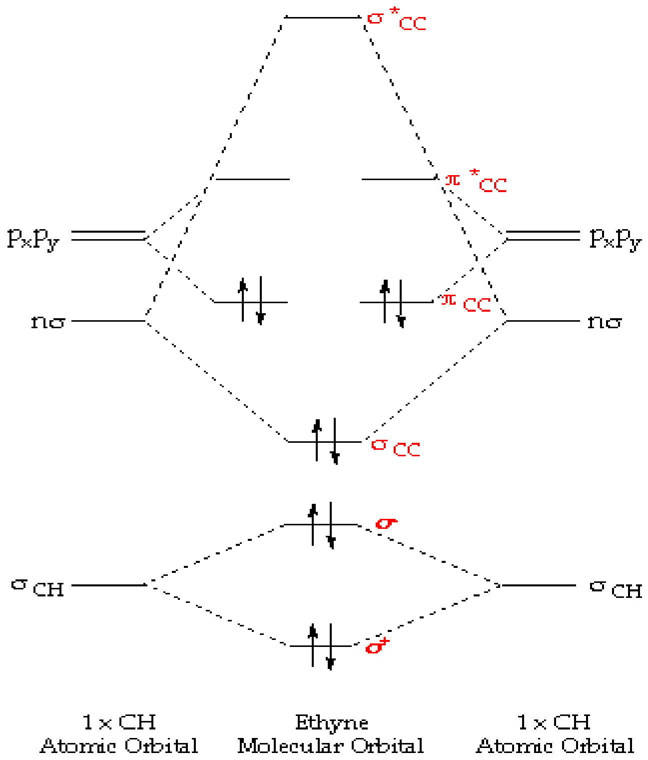


Figure 2.2.5: The molecular orbitals of ethyne show increasing nodal structure with increasing orbital energy. ***Source*****:** W. Locke and the ICSTM Department of Chemistry.

Molecules with electron lone pairs

Hydrogen Fluoride:

A simple diatomic molecule is Hydrogen fluoride. There are eight valence electrons which occupy four molecular orbitals. The two highest energy MO's are degenerate, are π-type and have no electron density associated with the hydrogen atom, *ie*. they are Non-Bonding Orbitals (**NBO**) and in Lewis Theory are represented as two "*Lone Pairs*". Another important difference between Hydrogen Fluoride and previous molecules is that the electron density is not equally distributed about the molecule. There is a much greater electron density around the fluorine atom. This is because fluorine is an extremely electronegative element, and in each bonding molecular orbital, fluorine will take a greater share of the electron density (W. Locke and the ICSTM, 1996,1997).

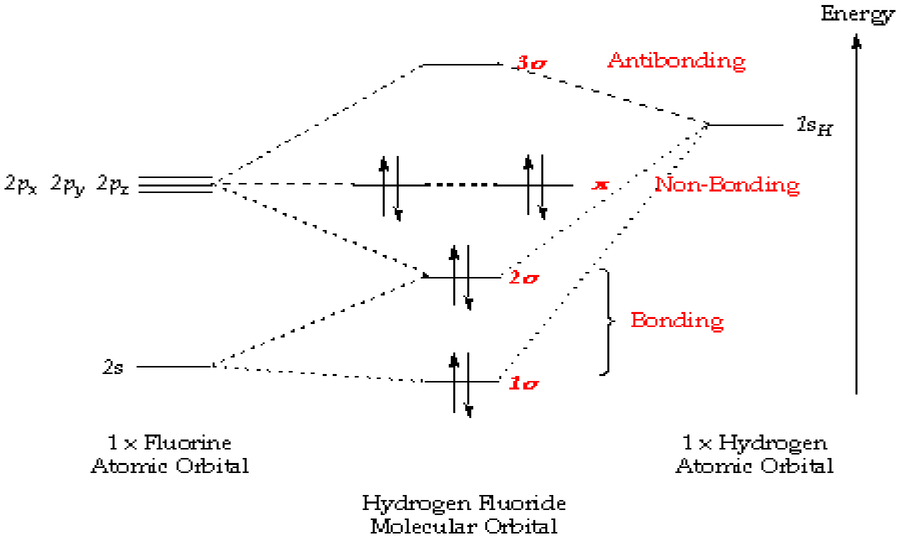


Figure 2.2.6: The molecular orbitals of hydrogen fluoride show increasing nodal structure with increasing orbital energy.*Source*: W. Locke and the ICSTM Department of Chemistry.

3.6 Valence bond model versus Molecular orbital theory

Because arguments based on atomic orbitals focus on the bonds formed between valence electrons on an atom, they are often said to involve a *valence-bond* theory.

The valence-bond model can't adequately explain the fact that some molecules contain two equivalent bonds with a bond order between that of a single bond and a double bond. The best it can do is suggests that these molecules are mixtures, or hybrids, of the two Lewis structures that can be written for these molecules.

This problem, and many others, can be overcome by using a more sophisticated model of bonding based on **molecular orbitals**. Molecular orbital theory is more powerful than valence-bond theory because the orbitals reflect the geometry of the molecule to which they are applied. But this power carries a significant cost in terms of the ease with which the model can be visualized.

3.7 Using the Molecular orbital model to explain why some molecules do not exist

This molecular orbital model can be used to explain why He_2 molecules don't exist. Combining a pair of helium atoms with $1s^2$ electron configurations would produce a molecule with a pair of electrons in both the σ bonding and the σ^* antibonding molecular orbitals. The total energy of a He_2 molecule would be essentially the same as the energy of a pair of isolated helium atoms, and there would be nothing to hold the helium atoms together to form a molecule.

The fact that a He_2 molecule is neither more nor less stable than a pair of isolated helium atoms illustrates an important principle: The core orbitals on an atom make no contribution to the stability of the molecules that contain this atom. The only orbitals that are important in our discussion of molecular orbitals are those formed when valence-shell orbitals are combined. The molecular orbital diagram for an O_2 molecule would therefore ignore the $1s$ electrons on both oxygen atoms and concentrate on the interactions between the $2s$ and $2p$ valence orbitals.

Activity B

Construct a molecular orbital diagram for the following molecules: (a) O_2 (b) H_2 (c) He_2

4.0 Conclusion

A molecular orbital describes the behaviour of one electron in the electric field generated by the nuclei and some average distribution of the other electrons.

5.0 Summary

In this unit, we have learnt that:

(i) **A molecular orbital** (MO) is a mathematical function that describes the wave-like behaviour of an electron in a molecule.

(ii) A molecular orbital (MO) can be used to specify the electron configuration of a molecule: the spatial distribution and energy of one (or one pair of) electron(s).

(iii) In molecules the valence electrons are found in MOs that are spread out over all atoms.

(iv) Molecular orbital theory is more powerful than valence-bond theory because the orbitals reflect the geometry of the molecule to which they are applied.

(v) The number of bonds between a pair of atoms is called the **bond order**. Bond orders can be calculated from Lewis structures, which are the heart of the valence-bond model.

6.0 Tutor marked assignment

1. Give the differences between valence bond theory and molecular orbital theory.
2. With a well illustrated diagram show the molecular orbital for each of the following molecules:

(a) Methane (b) Ethane (c) Ethene (d)Ethyne (e) Hydrogen fluoride (f) Ammonia

7.0 Further reading and other resources

Coulson, C.A. (1938). *Proc. Camb. Phil. Soc. 34*, 204.

Coulson, C. A. (1952). *Valence*. Oxford at the Clarendon Press.

Daintith, J. (2004). *Oxford Dictionary of Chemistry*. New York: Oxford University Press. ISBN 0-19-860918-3.

Hall, G.G. Lennard-Jones, Sir John. (1950). *Proc. Roy. Soc. A202*, 155.

Hückel, E. (1934). *Trans. Faraday Soc. 30*, 59.

Hund, F. (1926) "Zur Deutung einiger Erscheinungen in den Molekelspektren" [On the interpretation of some phenomena in molecular spectra] *Zeitschrift für Physik*, vol. 36, pages 657-67.

Hund, F. (1927) "Zur Deutung der Molekelspektren," *Zeitschrift für Physik*, Part I, vol. 40, pages 742-764 (1927); Part II, vol. 42, pages 93-120 (1927); Part III, vol. 43, pages 805-826 (1927); Part IV, vol. 51, pages 759-795 (1928); Part V, vol. 63, pages 719-751 (1930).

Hund, F. and Chemistry, (1996) Werner Kutzelnigg, on the occasion of Hund's 100th birthday, Angewandte Chemie, 35, 573 - 586, Imperial College London , Introduction to Molecular Orbital Theory. Retrieved August 2, 2009 from website: http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/02_1.wrl

Java molecular orbital. Retrieved August 2, 2009 from website: http://www.falstad.com/qmmol/

Jensen, F. (1999). Introduction to Computational Chemistry, John Wiley and Sons, , pg 65 - 69, ISBN 0 471 98055

Lennard-Jones, J. E.(1929) - Foundations of Molecular Orbital Theory. Retrieved August 2, 2009 from website: http://www.quantum-chemistry-history.com/LeJo-Dat

Lennard-Jones, J. E. (1929) "The electronic structure of some diatomic molecules," *Transactions of the Faraday Society*, vol. 25, pages 668-686.

Licker, Mark, J. (2004). *McGraw-Hill Concise Encyclopedia of Chemistry*. New York: McGraw-Hill. ISBN 0-07-143953-6.

Mulliken, R. (1966) Nobel Lecture- Spectroscopy, Molecular Orbitals, and Chemical Bonding - Retrieved August 2, 2009 from website: http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1996/Mulliken-lecture

Mulliken, R.S. (1927) "Electronic states. IV. Hund's theory; second positive nitrogen and Swan bands; alternate intensities," *Physical Review*, vol. 29, pages 637 - 649.

Mulliken, R.S. (1928) "The assignment of quantum numbers for electrons in molecules," *Physical Review*, vol. 32, pages 186 - 222.

Mulliken, R. S. (1967). Nobel Lecture, Science, 157, no. 3785, 13 - 24, (1967). Available on-line at: http://nobelprize.org/nobel_prizes/chemistry/laureates/1966/mulliken-lecture.pdf .

UC Berkeley video lecture on molecular orbitals Visualizations of some atomic and molecular orbitals. Retrieved August 2, 2009 from website: http://www.daugerresearch.com/orbital/

Wikipedia Encyclopedia. Retrieved August 2, 2009 from website: "http://en.wikipedia.org/wiki/Molecular_orbital"

W. Locke and the ICSTM Department of Chemistry 1996-97. Retrieved August 2, 2009 from

website: http://www.ch.ic.ac.uk/vchemlib/course/mo_theory/02_1.wrl

Module 2: Theory of chemical bonding

Unit 3: Resonance

Contents

1.0 Introduction 135

2.0 Objectives.. 136

3.0 Definition of Resonance 137
  3.1 Resonance as a diagrammatic tool 137
  3.2 A vector analogy 139
  3.3 True nature of resonance 139
  3.4 Resonance energy 140
  3.5 Steps to writing resonance structures 141
  3.6 Reactive intermediates 143
4.0 Conclusion 144
5.0 Summary 144
6.0 Tutor marked assignment 145
7.0 Further reading and other references 145

1.0 Introduction

The concept of resonance was introduced by Pauling in 1928. The term "resonance" came from the analogy between the quantum mechanical treatment of the H_2 molecule and a classical system consisting of two coupled oscillators. In the classical system, the coupling produces two modes, one of which is lower in frequency than either of the uncoupled vibrations; quantum-mechanically, this lower frequency is interpreted as a lower energy. The alternative term **mesomerism** popular in German and French publications with the same meaning was introduced by Christopher Ingold in 1938 but did not catch on in the English literature. The current concept of effect has taken on a related but different meaning. The double headed arrow was introduced by the German chemist Fritz Arndt who preferred the German phrase *zwischenstufe* or *intermediate phase*.

Due to confusion with the physical meaning of the word resonance, as no elements actually appear to be resonating, it has been suggested that the term resonance be abandoned in favor of **delocalization**. Resonance energy would become **delocalization energy** and a resonance structure becomes a **contributing structure**. The double headed arrows would be replaced by commas.

2.0 Objectives

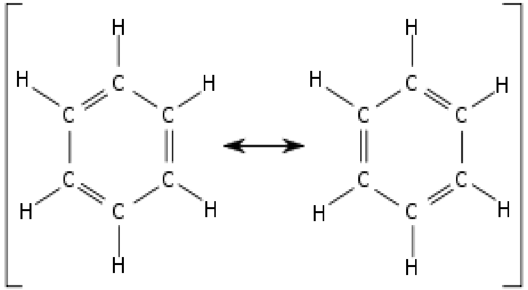
By the end of this unit, you should be able to:

a. define what resonance is;
b. draw resonance structures of different molecules;
c. explain what resonance energy is;
d. explain what reactive intermediates are and
e. explain what vector analogy of resonance is.

3.0 Definition of Resonance

Resonance in chemistry is a key component of valence bond theory used to graphically represent and mathematically model certain types of molecular structures when no single, conventional Lewis structure can satisfactorily represent the observed structure or explain its properties. Resonance instead considers such molecules to be an intermediate or average (called a **resonance hybrid**) between several Lewis structures that differ only in the placement of the valence electrons.

3.1 Resonance as a diagrammatic tool



Scheme 2.3.1. Resonance structures of benzene

A single Lewis structure often cannot represent the true electronic structure of a molecule. While one can only show an integral number of covalent bonds between two and only two atoms using these diagrams, one often finds that the experimentally deduced or calculated (from Quantum mechanics) structure of the molecule does not match any of the possible Lewis structures but rather has properties in some sense intermediate to these. Resonance structures are then employed to approximate the true electronic structure. Take the example of benzene (shown above, right). In a Lewis diagram, two carbons can be connected by one or two covalent bonds, but in the observed benzene molecule the carbon-carbon bond lengths are 139 pm, longer than typical C=C double bonds (133 pm) yet shorter than typical C-C single bonds (154 pm). More importantly, they are all equivalent, a fact no Lewis structure can explain. Therefore one calls the two Lewis structures canonical, contributing or resonating structures and the real molecule is considered to be their average, called a resonance hybrid. Resonance structures of the same molecule are connected with a double-headed arrow.

This form of resonance is simply a way of representing the structure graphically. It is only a notation and does not represent a real phenomenon. The individual resonance structures do not exist in reality: the molecule does not inter-convert between them. Instead, the molecule exists in a single unchanging state, intermediate between the resonance structures and only partially described by any one of them. This sharply distinguishes resonance from tautomerism. When it is said that a molecule is stabilized by resonance or that amides are less basic because the lone pair on nitrogen is involved in resonance with the carbonyl π electron, no phenomenon is implied. What is meant is simply that the molecule behaves differently from what we expect by looking at its Lewis structure because the structure diagrammed does not represent the actual structure of the molecule. From this viewpoint, the terminology treating resonance as something that 'happens' is perhaps an unfortunate historical burden.

It is also not correct to say that resonance occurs because electrons "flow", "circulate", or change their place within the molecules in a way described by classical physics, since this would produce a magnetic field, which is not observed. The fundamental description is that the electrons are in a quantum superposition of the two possibilities. There is probability amplitude to go back and forth between the two forms, but the two forms occur with equal probability amplitude so that the flows are balanced.

The quantum flows may be made imbalanced by applying an external magnetic field perpendicular to the plane of an aromatic ring. The magnetic field changes the phase for quantum hopping in the plane of the ring, and the amplitudes rearrange themselves so that they have a net flow in one direction. An opposing magnetic field appears, demonstrating that that the delocalized π electrons are truly spread out over the entire ring. The applied magnetic field induces a current density ("ring current") of circulating electrons in the π system; which is the source of the magnetic field. A common manifestation of this effect is the large chemical shift observed in the NMR spectrum of aromatic structures.

3.2 A vector analogy

An accurate analogy of resonance is given by the algebra of vectors. A vector **r** is written in component form as x**i**+y**j**+z**k** where x, y, and z are components and **i**, **j**, and **k** are the standard orthogonal Cartesian unit vectors. Just as the real vector **r** is neither **i**, nor **j**, nor **k**, but rather a combination of all three, a resonance hybrid is a conceptual combination of resonance structures. x, y, and z have no independent existence; they are considered only as a decomposition of **r** into easier-to-handle components, as is the case with resonance structures. In fact this analogy is very close to the reality, as will be made clear in the following section.

3.3 True nature of resonance

Though resonance is often introduced in such a diagrammatic form in elementary chemistry, it actually has a deeper significance in the mathematical formalism of valence bond theory (VB). When a molecule cannot be represented by the standard tools of valence bond theory (promotion, hybridization, orbital overlap, sigma and π bond formation) because no single structure predicted by VB can account for all the properties of the molecule, one invokes the concept of resonance. (Wikipedia, 2009)

Valence bond theory gives us a model for benzene where each carbon atom makes two sigma bonds with its neighbouring carbon atoms and one with a hydrogen atom. But since carbon is tetravalent, it has the ability to form one more bond. In VB it can form this extra bond with either of the neighbouring carbon atoms, giving rise to the familiar ring structure. But this cannot account for all carbon-carbon bond lengths being equal in benzene. A solution is to write the actual wavefunction of the molecule as a linear superposition of the two possible Kekulé structures (or rather the wavefunctions representing these structures), creating a wavefunction that is neither of its components but rather a superposition of them, just as in the vector analogy above (which is formally equivalent to this situation). In the mathematical discipline of graph theory, a Kekulé structure is a matching or edge-independent set in a graph

In benzene both Kekulé structures have equal weight, but this need not be the case. In general, the superposition is written with undetermined constant coefficients, which are then variationally optimized to find the lowest possible energy for the given set of basis wavefunctions. This is taken to be the best approximation that can be made to the real structure, though a better one may be made with addition of more structures.

In molecular orbital theory, the main alternative to VB, resonance often (but not always) translates to a delocalization of electrons in π orbitals (which are a separate concept from π bonds in VB). For example, in benzene, the MO model gives us 6 π electrons completely delocalised over all 6 carbon atoms, thus contributing something like half-bonds. This MO interpretation has inspired the picture of the benzene ring as a hexagon with a circle inside. Often when describing benzene the VB picture and the MO picture are intermixed, talking both about localized sigma 'bonds' (strictly a concept from VB) and 'delocalized' π electrons (strictly a concept from MO).

3.4 Resonance energy

Resonance hybrids are always more stable than any of the canonical structures would be, if they existed. The delocalization of the electrons lowers the orbital energies, imparting this stability. The resonance in benzene gives rise to the property of aromaticity. The gain in stability of the resonance hybrid over the most stable of the (non-existent) canonical structures is called the resonance energy (Wikipedia, 2009). A canonical structure that is lower in energy makes a relatively greater contribution to the resonance hybrid, or the actual picture of the molecule. In fact, resonance energy, and consequently stability, increases with the number of canonical structures possible, especially when these (non-existent) structures are equal in energy. Resonance energy of a conjugated system can be 'measured' by heat of hydrogenation of the molecule. Consider the example of benzene. The energy required to hydrogenate an isolated π-bond is around 28.6 kcal/mol (120 kJ/mol). Thus, according to the VB picture of benzene (having three π-bonds), the complete hydrogenation of benzene should require 85.8 kcal/mol (360 kJ/mol). However, the experimental heat of hydrogenation of benzene is around 49.8 kcal/mol (210 kJ/mol). The difference of 36 kcal/mol (150 kJ/mol) can be looked upon as a measure of resonance energy. One must bear in mind again that resonance structures have no physical existence. So, even though the term 'resonance energy' is quite meaningless, it offers an insight into how different the VB picture of a molecule is from the actual molecule itself. The resonance energy can be used to calculate on the Pauling scale.

Activity A

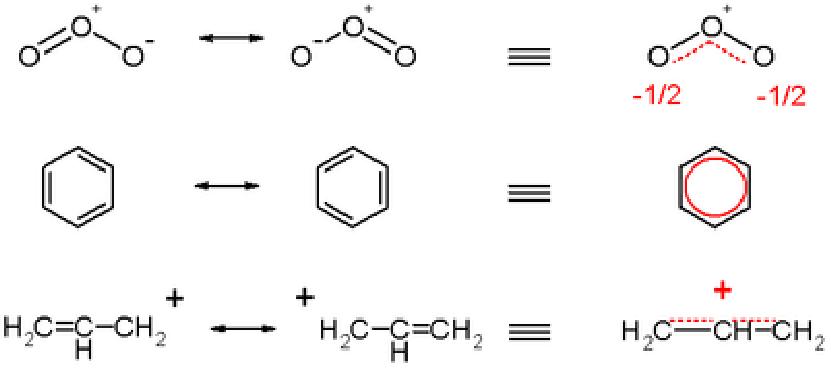
(a) define resonance;
(b) draw resonance structures of different molecules; and
(c) explain what resonance energy is

3.5 Steps to writing resonance structures (Wikipedia, 2009)

1. Position of nuclei must be the same in all structures; otherwise they would be isomers with real existence.

2. Total number of electrons and thus total charge must be constant.
3. When separating charge (giving rise to ions), usually structures where negative charges are on less electronegative elements have little contribution, but this may not be true if additional bonds are gained.
4. Resonance hybrids can not be made to have lower energy than the actual molecules.
5. Resonance hybrids must have the same number of unpaired electrons (if any)

Examples



Scheme 2.3.2. Examples of resonance - ozone, benzene and the allyl cation

Source: (Wikipedia, 2009)

The ozone molecule is represented by two resonance structures in the top of *scheme 2*. In reality the two terminal oxygen atoms are equivalent and the hybrid structure is drawn on the right with a charge of -1/2 on both oxygen atoms and partial double bonds.

The concept of benzene as a hybrid of two conventional structures (middle *scheme 2*) was a major breakthrough in chemistry made by , and the two forms of the ring which together represent the total resonance of the system are called *Kekulé structures*. In the hybrid structure on the right the circle replaces three double bonds, and represents six electrons in a set of three molecular orbitals of π symmetry, with a nodal plane in the plane of the molecule.

3.6 Reactive intermediates

Often, reactive intermediates such as and free radicals have more delocalised structure than their parent reactants, giving rise to unexpected products. The classical example is allylic rearrangement. When 1 mole of HCl adds to 1 mole of 1,3-butadiene, in addition to the ordinarily expected product 3-chloro-1-butene, we also find 1-chloro-2-butene. Isotope labelling experiments have shown that what happens here is that the additional double bond shifts from 1,2 position to 2,3 position in some of the product. This and other evidence (such as NMR in solutions) shows that the intermediate carbocation must have a highly delocalised structure, different from its mostly classical (delocalisation exists but is small) parent molecule. This cation (an allylic cation) can be represented using resonance, as shown above (Wikipedia, 2009).

This observation of greater delocalisation in less stable molecules is quite general. The excited states of conjugated are stabilised more by conjugation than their ground states, causing them to become organic dyes.

A well-studied example of delocalisation that does not involve π electrons ( ) can be observed in the non-classical ion cation. Other examples are and (CH_5^+). These are known as 3-center-2-electron bonds and are represented either by resonance structures involving rearrangement of sigma electrons or by a special notation, a Y that has the three nuclei at its three points.

4.0 Conclusion

Resonance hybrids are always more stable than any of the canonical structures would be, if they existed. The delocalization of the electrons lowers the orbital energies, imparting this stability. The resonance in benzene gives rise to the property of . The gain in stability of the resonance hybrid over the most stable of the (non-existent) canonical structures is called the resonance energy.

Activity B

(a) Explain what reactive intermediates are.
(b) Explain what vector analogy of resonance is.

5.0 Summary

In this unit we have learnt that;

(i) resonance in chemistry is used to graphically represent and mathematically model certain types of molecular structures when no single, conventional Lewis structure can satisfactorily represent the observed structure or explain its properties,
(ii) when a molecule cannot be represented by the standard tools of valence bond theory (promotion, hybridization, orbital overlap, sigma and π bond formation) because no single structure predicted by VB can account for all the properties of the molecule, one invokes the concept of resonance,
(iii)resonance hybrids are always more stable than any of the canonical structures would be, if they existed and

(iv)reactive intermediates such as and free radicals have more delocalised structure than their parent reactants, giving rise to unexpected products.

6.0 Tutor marked assignment

1. State the steps you would take in writing resonance structures.
2. Write resonance structures for each of the following (a) ozone, (b) benzene and (c) the allyl cation.
3. Explain what you understand by : (a) resonance energy and (b) reactive intermediates

7.0 Further reading and other references

Morrison,R. and Boyd,R. (1989). "Chapter 10". *Organic Chemistry* (Fifth Edition ed.). Prentice Hall of India. pp. 372. 0-87692-560-3.

Kerber, R.C *(***2006)** *If It's Resonance, What Is Resonating?*Journal of Chemical Education 83 223. Retrieved August 2, 2009 from website:http://www.jce.divched.org/Journal/issues/2006

Wikipedia Encyclopedia (2009). Retrieved August 2, 2009 from website: "http://en.wikipedia.org/wiki/Resonance_(chemistry)"

Module 2: Theory of chemical bonding

Unit 4: Angular momentum

Contents

1.0 Introduction 147

2.0 Objectives 147

3.0 Definition of angular momentum coupling 148

3.1 General theory and detailed origin....148

3.2 LS coupling....151

3.2.1 Spin-spin coupling....152

3.2.2 Orbit-Orbit coupling....152

3.2.3 Spin-orbit coupling....153

3.3 jj coupling....154

3.4 Term symbols 154

3.5 Nuclear coupling 155

4.0 Conclusion 157

5.0 Summary 157

6.0 Tutor marked assignment 158

7.0 Further reading and references 158

1.0 Introduction

Angular momentum is a property of a physical system that is a constant of motion (is time-independent and well-defined) in two situations: (i) the system experience a spherical symmetric potential field. (ii) The system moves (in quantum mechanical sense) in isotropic space. In both cases the angular momentum operator commutes with the Hamiltonian of the system. By Heisenberg's uncertainty relation this means that the angular momentum can assume a sharp value simultaneously with the energy (eigenvalue of the Hamiltonian) (Wikipedia, 2009).

2.0 Objectives

By the end of this unit, you should be able to:

(a) define what angular momentum is;
(b) explain angular momentum coupling;
(c) explain Russell-Saunders (or L - S) coupling and and

(d) j-j coupling.

3.0 Definition of angular momentum coupling

In quantum mechanics, the procedure of constructing eigenstates of total angular momentum out of eigenstates of separate angular momenta is called **angular momentum coupling**. For instance, the orbit and spin of a single particle can interact through spin-orbit interaction, in which case it is useful to couple the spin and orbit angular momentum of the particle. Or two charged particles, each with a well-defined angular momentum, may interact by Coulomb forces, in which case coupling of the two one-particle angular momenta to a total angular momentum is a useful step in the solution of the two-particle Schrödinger equation. In both cases the separate angular momenta are no longer constants of motion, but the sum of the two angular momenta usually still is. Angular momentum coupling in atoms is of importance in atomic spectroscopy. Angular momentum coupling of electron spins is of importance in quantum chemistry. Also in the nuclear shell model angular momentum coupling is ubiquitous.

General theory and detailed origin

Angular momentum is a property of a physical system that is a constant of motion (is time-independent and well-defined) in two situations: (i) The system experiences a spherical symmetric potential field. (ii) The system moves (in quantum mechanical sense) in isotropic space. In both cases the angular momentum operator commutes with the Hamiltonian of the system. By Heisenberg's uncertainty relation this means that the angular momentum can assume a sharp value simultaneously with the energy (eigenvalue of the Hamiltonian) (Wikipedia, 2009).

An example of the first situation is an atom whose electrons only feel the Coulomb field of its nucleus. If we ignore the electron-electron interaction (and other small interactions such as spin-orbit coupling), the orbital angular momentum **l** of each electron commutes with the total

Hamiltonian. In this model the atomic Hamiltonian is a sum of kinetic energies of the electrons and the spherical symmetric electron-nucleus interactions. The individual electron angular momenta **l**(i) commute with this Hamiltonian. That is, they are conserved properties of this approximate model of the atom (Wikipedia, 2009).

An example of the second situation is a rigid rotor moving in field-free space. A rigid rotor has a well-defined, time-independent, angular momentum.

These two situations originate in classical mechanics. The third kind of conserved angular momentum, associated with spin, does not have a classical counterpart. However, all rules of angular momentum coupling apply to spin as well.

In general the conservation of angular momentum implies full rotational symmetry (described by the groups SO(3) and SU(2)) and, conversely, spherical symmetry implies conservation of angular momentum. If two or more physical systems have conserved angular momenta, it can be useful to add these momenta to a total angular momentum of the combined system—a conserved property of the total system. The building of eigenstates of the total conserved angular momentum from the angular momentum eigenstates of the individual subsystems is referred to as angular momentum coupling (Wikipedia, 2009).

Application of angular momentum coupling is useful when there is an interaction between subsystems that, without interaction, would have conserved angular momentum. By the very interaction the spherical symmetry of the subsystems is broken, but the angular momentum of the total system remains a constant of motion. Use of the latter fact is helpful in the solution of the Schrödinger equation.

As an example we consider two electrons, 1 and 2, in an atom (say the helium atom). If there is no electron-electron interaction, but only electron nucleus interaction, the two electrons can be rotated around the nucleus independently of each other; nothing happens to their energy.

Both operators, **l**(1) and **l**(2), are conserved. However, if we switch on the electron-electron interaction depending on the distance *d*(1,2) between the electrons, then only a simultaneous and equal rotation of the two electrons will leave *d*(1,2) invariant. In such a case neither **l**(1) nor **l**(2) is a constant of motion but **L** = **l**(1) + **l**(2) is. Given eigenstates of **l**(1) and **l**(2), the construction of eigenstates of **L** (which still is conserved) is the *coupling of the angular momenta of electron 1 and 2*.

In quantum mechanics, coupling also exists between angular momenta belonging to different Hilbert spaces of a single object, *e.g.* its spin and its orbital angular momentum.

Reiterating slightly differently the above: one expands the quantum states of composed systems (*i.e.* made of subunits like two hydrogen atoms or two electrons) in basis sets which are made of direct products of quantum states which in turn describe the subsystems individually. We assume that the states of the subsystems can be chosen as eigenstates of their angular momentum operators (and of their component along any arbitrary *z* axis). The subsystems are therefore correctly described by a set of *l*, *m* quantum numbers (see angular momentum for details). When there is interaction between the subsystems, the total Hamiltonian contains terms that do not commute with the angular operators acting on the subsystems only. However, these terms *do* commute with the *total* angular momentum operator. Sometimes one refers to the non-commuting interaction terms in the Hamiltonian as *angular momentum coupling terms*, because they necessitate the angular momentum coupling.

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterise the electronic states of atoms.

There are two principal coupling schemes used:

- Russell-Saunders (or L - S) coupling and
- j-j coupling.

The interactions that can occur are of three types.

- spin-spin coupling
- orbit-orbit coupling
- spin-orbit coupling

3.2 LS coupling

In light atoms (generally Z<30), electron spins $\mathbf{s}_i$ interact among themselves so they combine to form a total spin angular momentum **S**. The same happens with orbital angular momenta $\mathbf{l}_i$, forming a single orbital angular momentum **L**. The interaction between the quantum numbers **L** and **S** is called **Russell-Saunders coupling** or **LS coupling**. Then **S** and **L** add together and form a total angular momentum **J**:

$\mathbf{J} = \mathbf{L} + \mathbf{S}$, where

$$\mathbf{L} = \sum_i \mathbf{l}_i$$ and

$$\mathbf{S} = \sum_i \mathbf{s}_i.$$

This is an approximation which is good as long as any external magnetic fields are weak. In larger magnetic fields, these two momenta decouple, giving rise to a different splitting pattern in the energy levels (the **Paschen-Back effect.**), and the size of LS coupling term becomes small (Wikipedia, 2009).

In the Russell Saunders scheme (named after Henry Norris Russell, 1877-1957 a Princeton Astronomer and Frederick Albert Saunders, 1875-1963 a Harvard Physicist and published in Astrophysics Journal, 61, 38, 1925) it is assumed that:
spin-spin coupling > orbit-orbit coupling > spin-orbit coupling.

This is found to give a good approximation for first row transition series where J coupling can generally be ignored, however for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used.

3.2.1 Spin-spin coupling

Spin-spin coupling is the coupling of the intrinsic angular momentum (spin) of different particles. Such coupling between pairs of nuclear spins is an important feature of nuclear magnetic resonance (NMR) spectroscopy as it can provide detailed information about the structure and conformation of molecules. Spin-spin coupling between nuclear spin and electronic spin is responsible for hyperfine structure in atomic spectra. S is the resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual m_s together and is as a result of coupling of spin quantum numbers for the separate electrons (Wikipedia, 2009).

3.2.2 Orbit-Orbit coupling

L - the total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows (Lancashire, 2006):

Total Orbital Momentum

L	0	1	2	3	4	5
	S	P	D	F	G	H

3.2.3 Spin-orbit coupling

The behavior of atoms and smaller particles is well described by the theory of quantum mechanics, in which each particle has an intrinsic angular momentum called spin and specific configurations (of e.g. electrons in an atom) are described by a set of quantum numbers. Collections of particles also have angular momenta and corresponding quantum numbers, and under different circumstances the angular momenta of the parts add in different ways to form the angular momentum of the whole. Angular momentum coupling is a category including some of the ways that subatomic particles can interact with each other (Wikipedia, 2009).

Spin-orbit coupling also known as **spin-pairing** describes a weak magnetic interaction, or coupling, of the particle spin and the orbital motion of this particle, e.g. the electron spin and its motion around an atomic nucleus. One of its effects is to separate the energy of internal states of the atom, e.g. spin-aligned and spin-antialigned that would otherwise be identical in energy. This interaction is responsible for many of the details of atomic structure (Wikipedia, 2009).

In the macroscopic world of orbital mechanics, the term ‘spin-orbit coupling’ is sometimes used in the same sense as spin-orbital resonance. Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the total angular momentum quantum number. Multiplicity occurs when several levels are close together and is given by the formula (2S+1).

The Russell Saunders term symbol that results from these considerations is given by:

$^{(2S+1)}L$

3.3 jj coupling

In heavier atoms the situation is different. In atoms with bigger nuclear charges, spin-orbit interactions are frequently as large or larger than spin-spin interactions or orbit-orbit interactions (Wikipedia, 2009). In this situation, each orbital angular momentum $\mathbf{l}_i$ tends to combine with each individual spin angular momentum $\mathbf{s}_i$, originating individual total angular momenta $\mathbf{j}_i$. These then add up to form the total angular momentum **J**

$$\mathbf{J} = \sum_i \mathbf{j}_i = \sum_i (\mathbf{l}_i + \mathbf{s}_i).$$

This description, facilitating calculation of this kind of interaction, is known as **jj coupling**.

3.4 Term symbols

Term symbols are used to represent the states and spectral transitions of atoms, they are found from coupling of angular momenta mentioned above. When the state of an atom has been specified with a term symbol, the allowed transitions can be found through selection rules by considering which transitions would conserve angular momentum. A photon has spin 1, and when there is a transition with emission or absorption of a photon the atom will need to change state to conserve angular momentum. The term symbol selection rules are. $\Delta S=0$, $\Delta L=0,\pm1$, $\Delta l=\pm1$, $\Delta J=0,\pm1$

3.5 Nuclear coupling

In atomic nuclei, the spin-orbit interaction is much stronger than for atomic electrons, and is incorporated directly into the nuclear shell model. In addition, unlike atomic-electron term symbols, the lowest energy state is not L - S, but rather, l + s. All nuclear levels whose l value (orbital angular momentum) is greater than zero are thus split in the shell model to create states designated by l + s and l - s. Due to the nature of the shell model, which assumes an average potential rather than a central Coulombic potential, the nucleons that go into the l + s and l - s nuclear states are considered degenerate within each orbital (e.g. The 2p3/2 contains four nucleons, all of the same energy. Higher in energy is the 2p1/2 which contains two equal-energy nucleons) (Wikipedia, 2009).

Activity A

(a) Define what angular momentum is.

(b) Explain what you understand by angular momentum coupling;.

3.6 Review of Quantum Numbers

Electrons in an atom reside in shells characterized by a particular value of n, the Principal quantum number. Within each shell an electron can occupy an orbital which is further characterized by an orbital quantum number, *l*, where *l* can take all values in the range:

$l = 0, 1, 2, 3, \ldots, (n-1)$,

traditionally termed s, p, d, f, etc. orbitals.

Each orbital has a characteristic shape reflecting the motion of the electron in that particular orbital, this motion being characterized by an angular momentum that reflects the angular velocity of the electron moving in its orbital.

A quantum mechanics approach to determining the energy of electrons in an element or ion is based on the results obtained by solving the Schrödinger Wave Equation for the H-atom. The various solutions for the different energy states are characterised by the three quantum numbers, n, l and m_l.

m_l is a subset of l, where the allowable values are: $m_l = l, l-1, l-2, \ldots 1, 0, -1, \ldots, -(l-2), -(l-1), -l$.

There are thus $(2l + 1)$ values of m_l for each l value,
i.e. one s orbital ($l = 0$), three p orbitals ($l = 1$), five d orbitals ($l = 2$), etc.

There is a fourth quantum number, m_s, that identifies the orientation of the spin of one electron relative to those of other electrons in the system. A single electron in free space has a fundamental property associated with it called spin, arising from the spinning of an asymmetrical charge distribution about its own axis. Like an electron moving in its orbital around a nucleus, the electron spinning about its axis has associated with its motion a well defined angular momentum. The value of m_s is either + ½ or - ½.
In summary then, each electron in an orbital is characterized by four quantum numbers (Lancashire, 2006):

Quantum Numbers	
n	Principal Quantum Number - largely governs size of orbital and its energy
l	Azimuthal/Orbital Quantum Number - largely determines shape of orbital

m_l	Magnetic Quantum Number
m_s	Spin Quantum Number - either + ½ or - ½ for single electron

Activity B

(a) Explain Russell-Saunders (or L - S) coupling.
(b) Explain j-j coupling.

4.0 Conclusion

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterise the electronic states of atoms.

5.0 Summary

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterize the electronic states of atoms.

There are two principal coupling schemes used: (i) Russell-Saunders (or L - S) coupling and (ii) j-j coupling.

The interactions that can occur are of three types: (i) spin-spin coupling (ii) orbit-orbit coupling and (iii) spin-orbit coupling

6.0 Tutor marked assignment

1. Explain the following terms and express each mathematically: (i) Rusell-Saunder's coupling (ii) jj coupling(iii) Nuclear coupling

2. Explain the following terms (i) spin-spin coupling (ii) orbit-orbit coupling and (iii) spin-orbit coupling

7.0 Further reading and references

Hund, F. (1925) *Zur Deutung verwickelter Spektren, insbesondere der Elemente Scandium bis Nickel.* [On the interpretation of complicated spectra, in particular the elements scandium through nickel]. Zeitschrift für Physik, vol. **33**, pp. 345-371.

Judd, B. R. (1967) *Atomic Shell Theory Recast*, Physical Review, vol. **162**, pp. 28-37

Lancashire, R.J. (2006). Retrieved August 2, 2009 from website: www.chem.uwimona.edu.jm/uwichem/chem.html

Nielson, C. W. and Koster, G. F. (1963) *Spectroscopic Coefficients for the* p^n, d^n, *and* f^n *Configurations*, MIT Press, Cambridge,.

URL http://wwwchem.uwimona.edu.jm/courses/RScoupling.html

Russell, H. N. and Saunders, F. A. (1925) *New Regularities in the Spectra of the Alkaline Earths*, Astrophysical Journal, vol. **61**, p. 38

Wikipedia, (2009). Wikipedia Encyclopedia Retrieved August 2, 2009 from website:http://en.wikipedia.org

Wormer, P. E. S. (1970) *Russell-Saunders States arising from configurations of equivalent electrons*, Chemical Physics Letters, vol. **5**, p. 355

"http://en.citizendium.org/wiki/Russell-Saunders_coupling"

Module 2: Theory of Chemical bonding

Unit 5: Bonds in Molecules

Contents

1.0 Introduction 160

2.0 Objectives 161

3.0 Definition of bonding 161

3.1Bond Order 163

3.2 Bond length 171

3.3 Bond energy 172

3.4 Bond dissociation energy 172

3.5 Force constant 172

3.6 Multiple bonds 172

4.0 Conclusion 175

5.0 Summary 175

6.0 Tutor marked assignment 175

7.0 Further readings and references 176

1.0 Introduction

The molecular orbital (MO) theory is a way of looking at the structure of a molecule by using *molecular* orbitals that belong to the molecule as a whole rather than to the individual atoms. When simple bonding occurs between two atoms, the pair of electrons forming the bond occupies an MO that is a mathematical combination of the wave functions of the atomic orbitals of the two atoms involved. The MO method originated in the work of Friedrich Hund and Robert S. Mulliken (Advameg, 2008).

2.0 Objectives

By the end of this Unit, you should be able to:

(a) define what bonding is;

(b) explain the difference between bonding and antibonding orbitals;

(c) draw Molecular orbital energy diagrams for diatomic molecules; and

(d) show the relationships between bond order and each of bond dissociation energy, bond length and force constant.

3.0 Definition of bonding

When atoms combine to form a molecule, the number of orbitals in the molecule equals the number of orbitals in the combining atoms. When two very simple atoms, each with one atomic orbital, are combined, two molecular orbitals are formed. One is a *bonding* orbital, lower in energy than the atomic orbitals, and derived from their sum. It is called *sigma*. The other is an *antibonding* orbital, higher in energy than the atomic orbitals, and resulting from their difference (Advameg, 2008). It is called *sigma-starred* (σ^*). (See the diagram in Figure 2.5.1.)

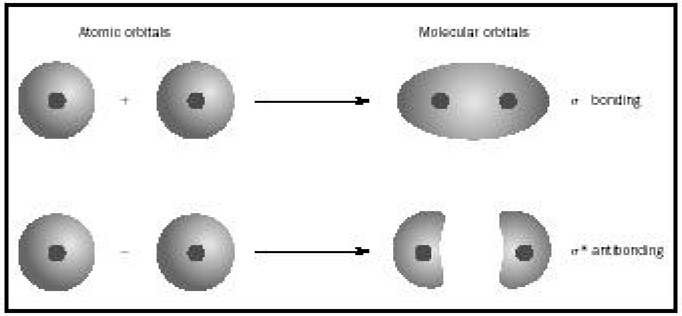


Figure 2.5.1. Combination of two 1s atomic orbitals to form a sigma bonding orbital or a sigma-starred antibonding orbital.

Source: www. Chemistryexplained.com/forum (Encyclopedia forum**)**

The basic idea might best be illustrated by considering diatomic molecules of hydrogen and helium. The energy diagrams are shown in Figure 2. Each hydrogen atom has one 1*s* electron. In the H_2 molecule the two hydrogen electrons go into the lowest energy MO available, the sigma orbital. In the case of helium, each helium atom has two electrons, so the He_2 molecule would have four. Two would go into the lower energy bonding orbital, but the other two would have to go into the higher energy sigma-starred orbital.

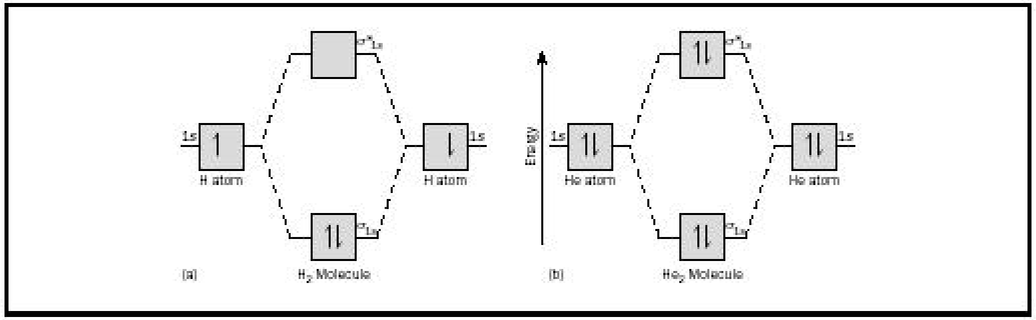


Figure 2.5.2. Molecular orbital energy diagrams for (a) H_2 showing both electrons in the bonding sigma MO; and (b) He_2 in which two of the electrons are in the antibonding sigma-starred MO. **Source: www.**Chemistryexplained.com/forum (Encyclopedia forum**)**

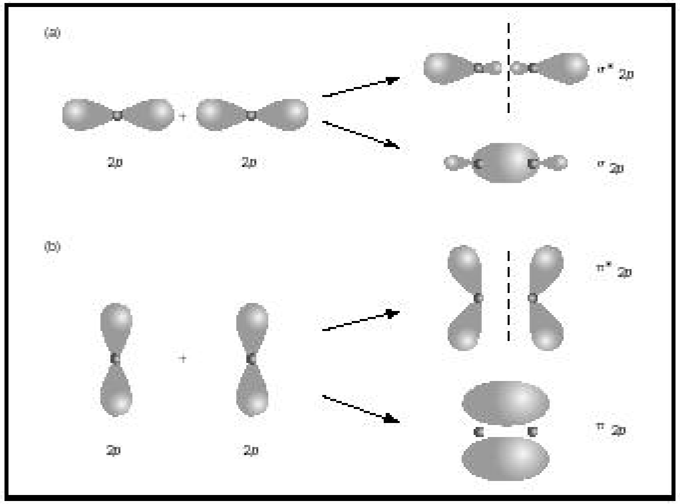
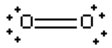


Figure 2.5.3. Combination of p atomic orbitals to form (a) sigma MOs by end-to-end interactions or (b) pi MOs by sideways interaction.

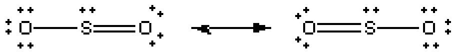
Source: www. Chemistryexplained.com/forum (Encyclopedia forum**)**

3.1 Bond order

The number of bonds between a pair of atoms is called the **bond order**. Bond orders can be calculated from Lewis structures, which are the heart of the valence-bond model. Oxygen, for example, has a bond order of two.



When there is more than one Lewis structure for a molecule, the bond order is an average of these structures (Advameg, 2008). The bond order in sulfur dioxide, for example, is 1.5 — the average of an S-O single bond in one Lewis structure and an S=O double bond in the other (Purdue, 2009).



In molecular orbital theory, we calculate bond orders by assuming that two electrons in a bonding molecular orbital contribute one net bond and that two electrons in an antibonding molecular orbital cancel the effect of one bond. We can calculate the bond order in the O_2 molecule by noting that there are eight valence electrons in bonding molecular orbitals and four valence electrons in antibonding molecular orbitals in the electron configuration of this molecule. Thus, the bond order is two.

$$\text{Bond order} = \frac{\text{bonding electrons} - \text{antibonding electrons}}{2} = \frac{8 - 4}{2} = 2$$

Although the Lewis structure and molecular orbital models of oxygen yield the same bond order, there is an important difference between these models. The electrons in the Lewis structure are all paired, but there are two unpaired electrons in the molecular orbital description of the molecule. As a result, we can test the predictions of these theories by studying the effect of a magnetic field on oxygen.

Atoms or molecules in which the electrons are paired are **diamagnetic** — repelled by both poles of a magnetic. Those that have one or more unpaired electrons are **paramagnetic** — attracted to a magnetic field. Liquid oxygen is attracted to a magnetic field and can actually bridge the gap between the poles of a horseshoe magnet. The molecular orbital model of O_2 is therefore superior to the valence-bond model, which cannot explain this property of oxygen.

The bond order for a molecule can be determined as follows:

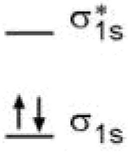
bond order = ½ (bonding electrons − antibonding electrons).

Therefore, the H_2 molecule has a bond order of ½ (2 − 0) = 1. In other words, there is a single bond connecting the two H atoms in the H_2 molecule. In the case of He_2, on the other hand, the bond order is ½ (2 − 2) = 0. This means that He_2 is not a stable molecule (Advameg, 2008).

We use bond orders to predict the stability of molecules. If the bond order for a molecule is equal to zero, the molecule is unstable. A bond order of greater than zero suggests a stable molecule. The higher the bond order is, the more stable the bond. We can use the molecular orbital diagram to predict whether the molecule is paramagnetic or diamagnetic. If all the electrons are paired, the molecule is diamagnetic. If one or more electrons are unpaired, the molecule is paramagnetic (Purdue, 2009).

Examples:

1. The molecular orbital diagram for a diatomic hydrogen molecule, H_2, is

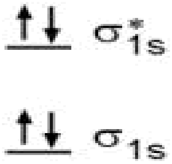


The bond order is 1. Bond Order = 1/2(2 - 0) = 1

The bond order above zero suggests that H_2 is stable.

Because there are no unpaired electrons, H_2 is diamagnetic.

2. The molecular orbital diagram for a diatomic helium molecule, He_2, shows the following.

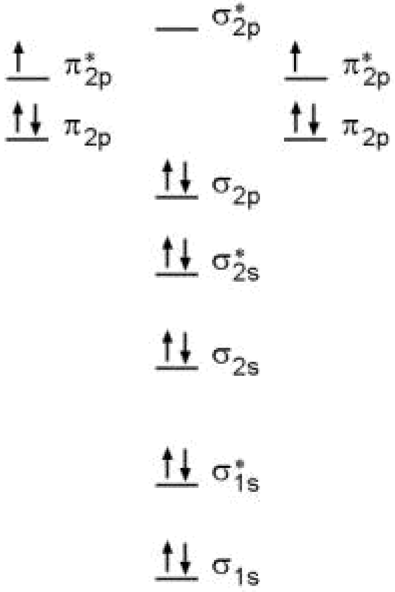


The bond order is 0 for He_2. Bond Order = 1/2(2 - 2) = 0

The zero bond order for He_2 suggests that He_2 is unstable.

If He_2 did form, it would be diamagnetic.

3. The molecular orbital diagram for a diatomic oxygen molecule, O_2, is

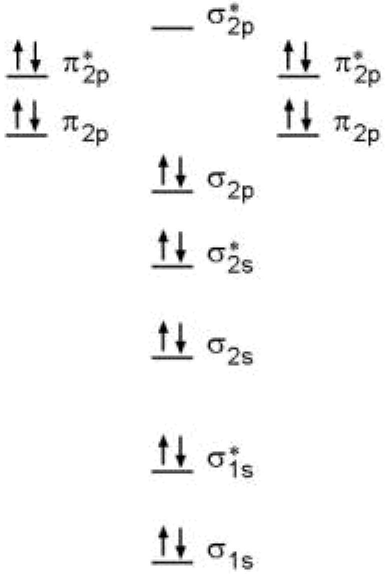


O_2 has a bond order of 2. Bond Order = 1/2(10 - 6) = 2

The bond order of two suggests that the oxygen molecule is stable.

The two unpaired electrons show that O_2 is paramagnetic.

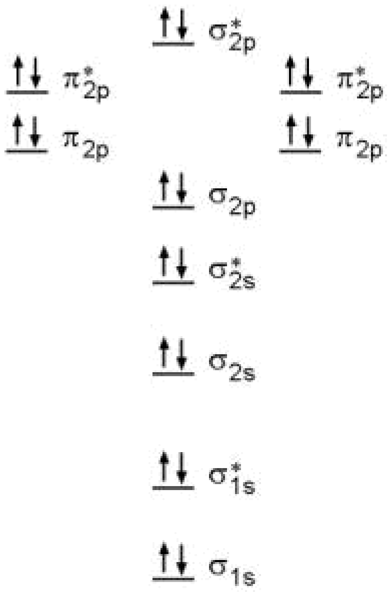
3. The molecular orbital diagram for a diatomic fluorine molecule, F_2, is



F_2 has a bond order of 1. Bond Order = 1/2(10 - 8) = 1

The bond order of one suggests that the fluorine molecule is stable. Because all of the electrons are paired, F_2 is diamagnetic.

4. The molecular orbital diagram for a diatomic neon molecule, Ne_2, is

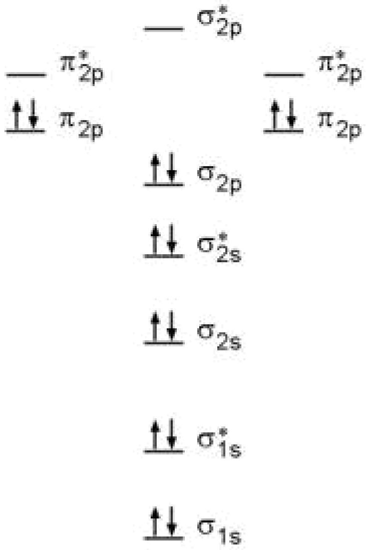


Ne_2 has a bond order of 0. Bond Order = 1/2(10 - 10) = 0

The zero bond order for Ne_2 suggests that Ne_2 is unstable. If Ne_2 did form, it would be diamagnetic (Mark, 2009).

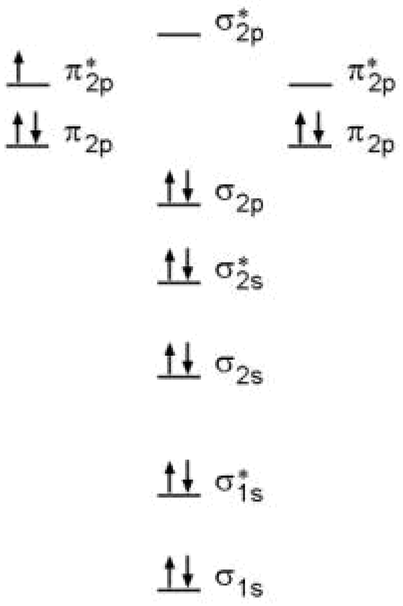
We can describe diatomic molecules composed of atoms of different elements in a similar way. The bond between the carbon and oxygen in carbon monoxide is very strong despite what looks like a strange and perhaps unstable Lewis Structure.

The plus formal charge on the more electronegative oxygen and the minus formal charge on the less electronegative carbon would suggest instability. The molecular orbital diagram predicts CO to be very stable with a bond order of three.



We predict the nitrogen monoxide molecule to be unstable according to the Lewis approach to bonding.

The unpaired electron and the lack of an octet of electrons around nitrogen would suggest an unstable molecule (Mark, 2009). NO is actually quite stable. The molecular orbital diagram predicts this by showing the molecule to have a bond order of 2.5.



Activity A

(a) Define the term bonding;

(b) Briefly explain the difference between bonding and antibonding orbitals;

3.2 Bond length

In molecular geometry, **bond length** or **bond distance** is the average distance between nuclei of two bonded atoms in a molecule. The qualitative relationship between bond order and bond length is that bond order is inversely proportional to bond length.

3.3 Bond energy

Bond energy is a measure of the strength of a chemical bond. The larger the bond energy, the stronger the bond. The bond energy is essentially the average enthalpy change for a gas reaction to break all the similar bonds. For the methane molecule, $C(-H)_4$, 435 kJ is required to break a single C-H bond for a mole of methane, but breaking all four C-H bonds for a mole requires 1662 kJ. Thus the average bond energy is (1662/4) 416 (not 436) kJ/mol.

3.4 Bond dissociation energy

The O–H bond of a water molecule (H–O–H) has 493.4 kJ mol^{-1} of bond dissociation energy, and 424.4 kJ mol^{-1} is needed to cleave the remaining O–H bond. The bond energy of the O–H bonds in water is 458.9 kJ mol^{-1}, which is the average of the values. The qualitative relationship between bond order and bond dissociation energy is that bond order is directly proportional to bond dissociation energy.

3.5 Force constant

The qualitative relationship between bond order and Force constant is that bond order is directly proportional to Force constant.

3.6 Multiple bonds

Double or triple bonds involve two or three pairs of bonding electrons. Single bonds are always sigma bonds, but in multiple bonds the first bond is sigma, while any second or third bonds are pi bonds. The overlap of *p* orbitals can yield either pi or sigma MOs, as shown in Figure 3. When they overlap end to end, they form sigma orbitals, but when they overlap side to side, they form pi orbitals.

Consider now the oxygen molecule. The Lewis structure for oxygen is :Ö::Ö: The double bond is necessary in order to satisfy the octet rule for both oxygen atoms. The measured bond length for oxygen supports the presence of a double bond. Yet we know that this Lewis formula cannot be the correct structure for oxygen because oxygen is paramagnetic, which means that the oxygen molecule must have unpaired electrons.

Look now at the MO diagram for oxygen, which is shown in Figure 4. It still indicates a bond order of 2 [$\frac{1}{2}(10-6) = 2$], but it also shows two unpaired electrons.

The MO theory also works well for larger molecules such as N_2O, CO_2, and BF_3 and for ions such as NO_3^- and CO_3^{2-}, in which the bonding MOs are delocalized, involving three or more atoms. It is especially useful for aromatic matic molecules such as benzene. In this case all six C atoms in the ring are equally involved in a delocalized pi electron cloud that envelops the entire molecule. The MO theory can even be extended to complex ions and to solids, including materials such as superconductors and semiconductors (Advameg, 2008).

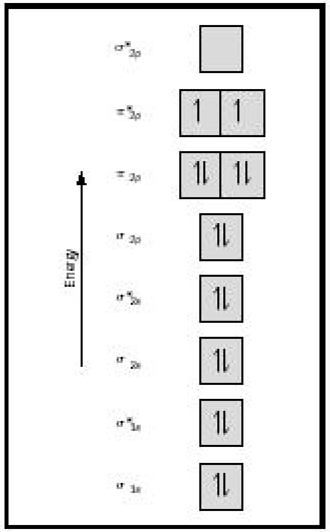


Figure 2.5.4. MO energy diagram for O_2. Eight electrons from each oxygen atom add up to 16 electrons in the O_2 molecule. They combine to form the molecular orbitals indicated above. **Source: www.**Chemistryexplained.com/forum (Encyclopedia forum**)**

Activity B

(c) Briefly define bond order and show the relationships between it and each of bond dissociation energy, bond length and force constant.

(d) Draw Molecular orbital energy diagrams for diatomic molecules;

4.0 Conclusion

When atoms combine to form a molecule, the number of orbitals in the molecule equals the number of orbitals in the combining atoms.

5.0 Summary

In this Unit, we have learnt that;

When simple bonding occurs between two atoms, the pair of electrons forming the bond occupies an MO that is a mathematical combination of the wave functions of the atomic orbitals of the two atoms involved.

(i) When molecular orbitals are formed, one is a *bonding* orbital, lower in energy than the atomic orbitals, and derived from their sum. It is called *sigma*. The other is an *antibonding* orbital, higher in energy than the atomic orbitals, and resulting from their difference. It is called *sigma-starred* (σ*).

(ii) Double or triple bonds involve two or three pairs of bonding electrons.

(iii) Single bonds are always sigma bonds, but in multiple bonds the first bond is sigma, while any second or third bonds are pi bonds.

6.0 Tutor marked assignment

1. Show the Molecular orbital energy diagrams for (a) H_2 showing both electrons in the bonding sigma MO; and (b) He_2 in which two of the electrons are in the antibonding sigma-starred MO.
2. Illustrate the combination of p atomic orbitals to form (a) sigma MOs by end-to-end interactions or (b) pi MOs by sideways interaction.

7.0 Further readings and references

Advameg (2008). Wiley.Search the Chemistry Explained powered by JRank, Advameg Inc. Retrieved August 6, 2009 from website: www.chemistryexplained.com/forum (encyclopedia forum)

Chang, R. (2002). *Chemistry*, 7th edition. New York: McGraw Hill.

deKock, R. L., and Gray, H. B. (1980). *Chemical Structure and Bonding*. Menlo Park, CA: Benjamin/Cummings.

Levine, Ira N. (1991). *Quantum Chemistry*, 4th edition. Englewood Cliffs, NJ: Prentice Hall.

Mark, B. (2009). Retrieved August 6, 2009 from website:www.mpcfaculty.net/mark_bishop

Solomons, T. W. G. (1997). *Fundamentals of Organic Chemistry*, 5th edition. New York: John

Module 3: Quantum Mechanics

Unit 1: Introduction to Quantum Chemistry

Contents

1.0 Introduction 179

2.0 Objectives 179

3.1 Definition of Quantum chemistry 179

  3.1 History of quantum mechanics 180

3.2 Electronic structure 181

3.3 Wave model 181

3.4 Valence bond 182

3.5 Molecular orbital 182

3.6 Density functional theory 182

3.7 Chemical dynamics 183

3.8 Adiabatic chemical dynamics 183

3.9 Non-adiabatic chemical dynamics 183

3.10 Quantum chemistry and quantum field theory 184

3.11 Usefulness of quantum mechanics 184

3.12 The postulates of quantum mechanics 185

3.13 Commutation of operators 186

3.14 Linearity of an operator 187

4.0 Conclusion 188

5.0 Summary 188

6.0 Tutor marked assignment 189

7.0 Further reading and references 189

1.0 Introduction

Quantum chemistry mathematically describes the fundamental behavior of matter at the molecular scale. It is, in principle, possible to describe all chemical systems using this theory. In practice, only the simplest chemical systems may realistically be investigated in purely quantum mechanical terms, and approximations must be made for most practical purposes (Wikipedia, 2009).

2.0 Objectives

By the end of this unit, you should be able to:

(a) define quantum chemistry;
(b) explain the history of quantum chemistry;
(c) explain the Usefulness of quantum mechanics;
(d) give the postulates of quantum mechanics and
(e) define an operator.

3.0 Definition of Quantum chemistry

Quantum chemistry is the application of **quantum mechanical** principles and equations to the study of molecules. In order to understand matter at its most fundamental level, we must use quantum mechanical models and methods. There are two aspects of quantum mechanics that make it different from previous models of matter. The first is the concept of wave-particle duality; that is, the notion that we need to think of very small objects (such as electrons) as having characteristics of both particles and waves. Second, quantum mechanical models correctly predict that the energy of atoms and molecules is always quantized, meaning that they may have only specific amounts of energy. Quantum chemical theories allow us to explain the structure of the periodic table, and quantum chemical calculations allow us to accurately predict the structures of molecules and the spectroscopic behavior of atoms and molecules.

Quantum chemistry is a branch of theoretical chemistry, which applies quantum mechanics and quantum field theory to address issues and problems in chemistry (Wikipedia, 2009). The description of the electronic behavior of atoms and molecules as pertaining to their reactivity is one of the applications of quantum chemistry. Quantum chemistry lies on the border between chemistry and physics, and significant contributions have been made by scientists from both fields. It has a strong and active overlap with the field of atomic physics and molecular physics, as well as physical chemistry.

In quantum mechanics the Hamiltonian, or the physical state, of a particle can be expressed as the sum of two operators, one corresponding to kinetic energy and the other to potential energy. The Hamiltonian in the Schrödinger wave equation used in quantum chemistry does not contain terms for the spin of the electron.

Solutions of the Schrödinger equation for the hydrogen atom gives the form of the wave function for atomic orbitals, and the relative energy of the various orbitals. The orbital approximation can be used to understand the other atoms e.g. helium, lithium and carbon.

3.1 History of quantum mechanics

The history of quantum chemistry essentially began with the 1838 discovery of cathode rays by Michael Faraday. The 1859 statement of the black body radiation problem by Gustav Kirchhoff, the 1877 suggestion by Ludwig Boltzmann that the energy states of a physical system could be discrete, and the 1900 quantum hypothesis by Max Planck that any energy radiating atomic system can theoretically be divided into a number of discrete energy elements ε such that each of these energy elements is proportional to the frequency v with which they each individually radiate energy, as defined by the following formula:

$$\epsilon = h\nu$$

where h is a numerical value called Planck's Constant. Then, in 1905, to explain the photoelectric effect (1839), i.e., that shining light on certain materials can function to eject electrons from the material, Albert Einstein postulated, based on Planck's quantum hypothesis, that light itself consists of individual quantum particles, which later came to be called photons (1926). In the years to follow, this theoretical basis slowly began to be applied to chemical structure, reactivity, and bonding (Wikipedia, 2009).

3.2 Electronic structure

The first step in solving a quantum chemical problem is usually solving the Schrödinger equation (or Dirac equation in relativistic quantum chemistry) with the electronic molecular Hamiltonian. This is called determining the electronic structure of the molecule. It can be said that the electronic structure of a molecule or crystal implies essentially its chemical properties. An exact solution for the Schrödinger equation can only be obtained for the hydrogen atom. Since all other atomic, or molecular systems, involve the motions of three or more "particles", their Schrödinger equations cannot be solved exactly and so approximate solutions must be sought (Wikipedia, 2009).

3.3 Wave model

The foundation of quantum mechanics and quantum chemistry is the wave model, in which the atom is a small, dense, positively charged nucleus surrounded by electrons. Unlike the earlier Bohr model of the atom, however, the wave model describes electrons as "clouds" moving in orbitals, and their positions are represented by probability distributions rather than discrete points. The strength of this model lies in its predictive power. Specifically, it predicts the pattern of chemically similar elements found in the periodic table. The wave model is so named because electrons exhibit properties (such as interference) traditionally associated with waves. See wave-particle duality (Wikipedia, 2009).

3.4 Valence bond

Although the mathematical basis of quantum chemistry had been laid by Schrödinger in 1926, it is generally accepted that the first true calculation in quantum chemistry was that of the German physicists Walter Heitler and Fritz London on the hydrogen (H_2) molecule in 1927. Heitler and London's method was extended by the American theoretical physicist John C. Slater and the American theoretical chemist Linus Pauling to become the **Valence-Bond (VB)** [or **Heitler-London-Slater-Pauling (HLSP)**] method. In this method, attention is primarily devoted to the pairwise interactions between atoms, and this method therefore correlates closely with classical chemists' drawings of bonds (Wikipedia, 2009).

3.5 Molecular orbital

An alternative approach was developed in 1929 by Friedrich Hund and Robert S. Mulliken, in which electrons are described by mathematical functions delocalized over an entire molecule. The **Hund-Mulliken** approach or **molecular orbital (MO) method** is less intuitive to chemists, but has turned out capable of predicting spectroscopic properties better than the VB method. This approach is the conceptional basis of the **Hartree-Fock method** and further post Hartree-Fock methods.

3.6 Density functional theory

The **Thomas-Fermi model** was developed independently by Thomas and Fermi in 1927. This was the first attempt to describe many-electron systems on the basis of electronic density instead of wave functions, although it was not very successful in the treatment of entire molecules. The method did provide the basis for what is now known as **density functional theory**. Though this method is less developed than post Hartree-Fock methods, its lower computational requirements allow it to tackle larger polyatomic molecules and even macromolecules, which has made it the most used method in computational chemistry at present (Wikipedia, 2009).

3.7 Chemical dynamics

A further step can consist of solving the Schrödinger equation with the total molecular Hamiltonian in order to study the motion of molecules. Direct solution of the Schrödinger equation is called *quantum molecular dynamics*, within the semiclassical approximation *semiclassical molecular dynamics*, and within the classical mechanics framework *molecular dynamics (MD)*. Statistical approaches, using for example Monte Carlo methods, are also possible.

3.8 Adiabatic chemical dynamics

In **adiabatic dynamics**, interatomic interactions are represented by single scalar potentials called potential energy surfaces. This is the Born-Oppenheimer approximation introduced by Born and Oppenheimer in 1927. Pioneering applications of this in chemistry were performed by Rice and Ramsperger in 1927 and Kassel in 1928, and generalized into the RRKM theory in 1952 by Marcus who took the transition state theory developed by Eyring in 1935 into account. These methods enable simple estimates of unimolecular reaction rates from a few characteristics of the potential surface.

3.9 Non-adiabatic chemical dynamics

Non-adiabatic dynamics consists of taking the interaction between several coupled potential energy surfaces (corresponding to different electronic quantum states of the molecule). The coupling terms are called vibronic couplings. The pioneering work in this field was done by Stueckelberg, Landau, and Zener in the 1930s, in their work on what is now known as the Landau-Zener transition. Their formula allows the transition probability between two diabatic potential curves in the neighborhood of an avoided crossing to be calculated.

3.10 Quantum chemistry and quantum field theory

The application of quantum field theory (QFT) to chemical systems and theories has become increasingly common in the modern physical sciences. One of the first and most fundamentally explicit appearances of this is seen in the theory of the photomagneton. In this system, plasmas, which are ubiquitous in both physics and chemistry, are studied in order to determine the basic quantization of the underlying bosonic field. However, quantum field theory is of interest in many fields of chemistry, including: nuclear chemistry, astrochemistry, sonochemistry, and quantum hydrodynamics. Field theoretic methods have also been critical in developing the ab initio Effective Hamiltonian theory of semi-empirical pi-electron methods (Wikipedia, 2009).

Activity A

(a) Define quantum chemistry;
(b) Explain the history of quantum chemistry;

3.11 Usefulness of quantum mechanics

The development of quantum mechanics has led to the possibility of calculating energy levels and other properties of and molecules. Its application has made it possible to understand the nature of chemical bonds. It also provides the basis for understanding spectroscopy (the study of interaction of electromagnetic radiation of electromagnetic radiation with molecules). In summary, the quantum theory is the basis of all our notions about the make-up of atoms and molecules, the building blocks of nature.

3.12 The postulates of quantum mechanics

Quantum mechanics is based on a set if unproved assumptions called postulates. These are validated by the extent to which the laboratory measurements agree with the calculated results. The postulates are:

Postulates 1

A quantum mechanical system is described as completely as possible when a function φ, called the wave function exists or is specified. For any physical situation, φ must be finite, single-valued and continuous. The particular values of φ satisfying equation below are called eigen functions while the values of the energy corresponding to these are called eigenvalues of the system.

$$\frac{d^2\varphi}{dx^2} = -\frac{2m}{\hbar^2}[E - U(x)]\varphi(x)$$

The physical significance of φ is vague but φ^2 or φφ* where φ* is the complex conjugate of φ and can be interpreted as the probability of finding a particle within a specified domain. For a one dimensional system, the domain is the interval: x and x+dx; for a two-dimensional problem or system, an element of area is required whereas for a three-dimensional problem or system, an element of volume is required. It is presumed that

$\int_{-\infty}^{\infty} \varphi\varphi^* d\tau$

exists where $d\tau = dxdydz$

and that φ is normalised by requiring that $\int^{\infty}_{-\infty} \varphi\varphi^* d\tau = 1$.

That means the integral of $\varphi\varphi^*$ over all space is 1.

Postulates 2

To every observable physical quantity of a given system, A, for example, there exists a corresponding linear operator, $\hat{A}$ such that

$\hat{A}\varphi = A\varphi$

A is the eigenvalue, φ is the eigenfunction and $\hat{A}$, the operator. An operator is a symbol that instructs one to do something. It is used in mathematical manipulation. For example, the symbol d/dx, which instructs you to take the derivative with respect to x of whatever follows the symbol. Operators are often denoted by superscript symbol, ^.

3.13 Commutation of operators

Two operators $\hat{A}$ and $\hat{G}$ commute if $\hat{A}\hat{G} = \hat{G}\hat{A}$

Example

Suppose $\hat{A}=d/dx$, $\hat{G}=x$ and $f(x) = x^3$ do the operators commute?

For the operators to commute $\hat{A}\hat{G}f(x)= \hat{G}\hat{A}f(x)$

$\hat{A}\hat{G}f(x)= d(x.\ x^3)/dx = d(x^4)/dx = 4x^3$

$\hat{G}\hat{A}f(x) = xd(x^3)/dx = 3x^2.x=3x^3$

Since $3x^3 \neq 4x^3$, the operators do not commute

3.14 Linearity of an operator

An operator is linear if $\hat{A}(a\varphi+b\text{Ø}) = a\hat{A}\varphi + b\hat{A}\text{Ø}$

Where a, b are constants and φ, Ø are arbitrary constants.

Postulates 3

If φ_1 and φ_2 represent possible states of a system, so does a linear combination of them, such that

$$\varphi_3 = a\varphi_1 + b\varphi_2$$

where a, b are constants.

Activity B

1. Briefly explain the following terms; (a) Postulate (b) Operator
2. Explain the Usefulness of quantum mechanics;
3. Give the postulates of quantum mechanics;

4.0 Conclusion

The quantum theory is the basis of all our notions about the make-up of atoms and molecules, the building blocks of nature.

5.0 Summary

In this unit we have learnt that:

(i) the description of the electronic behavior of atoms and molecules as pertaining to their reactivity is one of the applications of quantum chemistry.

(ii) solutions of the Schrödinger equation for the hydrogen atom gives the form of the wave function for atomic orbitals, and the relative energy of the various orbitals.

(iii) the foundation of quantum mechanics and quantum chemistry is the wave model, in which the atom is a small, dense, positively charged nucleus surrounded by electrons.

(iv) the development of quantum mechanics has led to the possibility of calculating energy levels and other properties of and molecules.

(v) quantum mechanics is based on a set if unproved assumptions called postulates.

6.0 Tutor marked assignment

1. why is the study of quantum mechanics necessary for you as a Chemist?
2. state and explain the postulates of quantum mechanics.
3. explain what you understand by each of the following terms: (a) Commutation of operators (b) Linearity of an operator.

7.0 Further reading and references

Atkins, P.W. *Physical Chemistry* (Oxford University Press) ISBN 0-19-879285-9

ChemViz Curriculum Support Resources. Retrieved August 2, 2009 from website: http://www.shodor.org/chemviz/

Early ideas in the history of quantum chemistry. Retrieved August 2, 2009 from website: http://www.quantum-chemistry.com/

Eric R. Scerri, The Periodic Table: Its Story and Its Significance, Oxford University Press, 2006. Considers the extent to which chemistry and especially the periodic system has been reduced to quantum mechanics. ISBN 0-19-530573-6.

Landau, L.D. and Lifshitz, E.M. *Quantum Mechanics:Non-relativistic Theory* (Course of Theoretical Physics vol.3) (Pergamon Press)

McWeeny, R. *Coulson's Valence* (Oxford Science Publications) ISBN 0-19-855144-4

Pauling, L. (1954). *General Chemistry*. Dover Publications. ISBN 0-486-65622-5.

Pauling, L., and Wilson, E. B. *Introduction to Quantum Mechanics with Applications to Chemistry* (Dover Publications) ISBN 0-486-64871-0

Pullman, B. and Pullman, A. (1963). *Quantum Biochemist.*, New York and London, Academic Press.

Quantum Chemistry". Retrieved August 2, 2009 from *The NIH Guide to Molecular Modeling*. National Institutes of Health website: http://cmm.cit.nih.gov/modeling/guide_documents/quantum_mechanics_document.html.

Simon, Z. 1976. *Quantum Biochemistry and Specific Interactions.*, Taylor & Francis; ISBN 978-0856260872 and ISBN 0-85-6260878 .

The Sherrill Group - Notes. Retrieved August 2, 2009 from website: http://vergil.chemistry.gatech.edu/notes/

Wikipedia (2009). Wikipedia Encyclopedia. Retrieved August 2, 2009 from website: http://en.wikipedia.org

Module 3: Quantum Mechanics

Unit 2: Orbitals, States and Wavefunctions

Contents

1.0 Introduction 192

2.0 Objectives 192

3.0 Definition of wavefunction 193

  3.1 Energy levels (n) 193

  3.2 Nature of wavefunction 194

  3.3 Wave properties of matter 195

  3.4 Application of De Broglie conjecture 197

4.0 Conclusion 200

5.0 Summary 200

6.0 Tutor marked assignment 201

7.0 Further reading and references 201

1.0 Introduction

For a scientist, knowing that matter behaves as a wave is useful only if one knows something about that wave. In 1926 Erwin Schrödinger introduced a mathematical equation whereby, if one knows the potential energy acting on an object, one can calculate the wavefunction for that object. Heisenberg had already introduced a mathematical formalism for performing quantum mechanics calculations, without explicitly including the concept of waves. It was later shown that, although the approaches of Schrödinger and Heisenberg looked very different, they made exactly the same predictions. In practice, the Schrödinger formalism is more useful for explaining the problem being studied, and the Heisenberg methodology allows for more straightforward computation. Accordingly, a mixture of the two approaches is typically used in modern quantum chemistry. Once we know the wavefunction of the atom or molecule under study, we can calculate the properties of that atom or molecule.

2.0 Objectives

By the end of this Unit, you should be able to:

(a) define wavefunction;

(b) explain the usefulness of wavefunction;

(c) nature of wavefunction and

(d) uncertainty principle

3.0 Definition of wavefunction

The wavefunction is a mathematical function describing the wave. For example, $y(x) = A \sin(kx)$ might be the wave-function for a one-dimensional wave, which exists along the x-axis. Matter waves are three-dimensional; the relevant wavefunction depends on the x, y, and z coordinates of the system being studied (and sometimes on time as well). We conventionally label the wavefunction for a three-dimensional object as $\psi(x, y, z)$.

Since electrons are fermions they are subject to the Pauli exclusion principle, which states that no two fermions can occupy the same quantum state at once. This is the fundamental basis of the configuration of electrons in an atom: once a state is occupied by an electron, the next electron must occupy a different quantum mechanical state.

In an atom, the stationary states of an electron's wavefunction (i.e. the states which are eigenstates of the Schrodinger equation [$H\Psi = E\Psi$, where H is the Hamiltonian] are referred to as **orbitals**, by analogy with the classical picture of electron particles orbiting the nucleus. In general, an orbital represents the region where an electron can be expected to exist (with ~90% probability). These states have four principal quantum numbers: n, l, m_l and m_s, and by the Pauli principle no two electrons may share the same values for all four numbers. The two most important of these are n and l.

3.1 Energy levels (n)

The first quantum number n corresponds to the overall energy and hence also the distance from the nucleus of an orbital, hence sets of states with the same n are often referred to as electron shells or energy levels. These are not sharply delineated zones within the atom, but rather fuzzy-edged regions within which an electron is likely to be found, due to the probabilistic nature of quantum mechanical wavefunctions.

Any discussion of the shapes of electron orbitals is necessarily imprecise, because a given electron, regardless of which orbital it occupies, can at any moment be found at any distance from the nucleus and in any direction due to the uncertainty principle.

However, the electron is much more likely to be found in certain regions of the atom than in others. Given this, a *boundary surface* can be drawn so that the electron has a high probability to be found anywhere within the surface, and all regions outside the surface have low values. The precise placement of the surface is arbitrary, but any reasonably compact determination must follow a pattern specified by the behavior of ψ^2, the square of the wavefunction. This boundary surface is what is meant when the "shape" of an orbital is mentioned.

3.2 Nature of wavefunction

The wavefunction ψ is a sort of amplitude fucntion. It is not an observable quantity but ψ ψ^* is observable where $\psi^*$is the conjugate of ψ. If the function is equal to its conjugate than ψ^2 gives the probability of finding the electron within a given volume. Where ψ^2 is high the probability of finding the electron is high. Where ψ^2 is low, the electron is rarely found. The information contained in ψ^2 can be likened to the information contained in the in a dart board. The pattern of holes shows that there is a high probability that the dart will land within a circle containing many dart holes and a low probability for a circle of equal area but containing few dart holes. The density of dart holes gives probability distribution.

The wave function ψ must obey certain mathematical conditions, that is, ψ(x) be single valued, finite and continuous for all physically possible values of x. It must be single valued because the probability of finding the electron at any point x must have only one value. It cannot be finite at any point because this would mean that it is fixed exactly at point. This is inconsistent with the wave properties. The criterion of continuous wave function is helpful in the selection of physically feasible solutions for the wave function.

3.3 Wave properties of matter

The idea that particles could exhibit wave properties just as wave could exhibit particle properties got serious attention in the 1920s when Louis de Broglie proposed in his doctoral thesis that particles in motion possessed a wavelength an could therefore act like waves. De Broglie obtained an expression for the wavelength of a particle by drawing an analogy to the behaviour of photons (Porlie, 1987). The relationship between the energy of the photon and its wavelength is given as

$\epsilon_{\gamma} = hc/\lambda$ …………………….(3.2.1)

Where h is Planck's constant, c the velocity of light and λ the wavelength the photon.

The energy of the a particle and its momentum (p) are related by

$\epsilon_{\gamma} = pc$ ……………………….. (3.2.2)

The relation between the momentum and the wavelength of a photon is

$p = h/\lambda$ …………………….. (3.2.3)

For a particle of mass *m*, the momentum is given as

$p = mv$ ………………………. (3.2.4)

According to de Broglie the momentum of the photon and that of the particle should be equal. That means the wavelength of the particle should be

$\lambda = h/p = h/mv$ ……………….………….. (3.2.5)

The equation represents a completely different view of the behaviour of particles such as the electron, which had been thought to possess only corpuscular properties.

The wave nature of particles and the quantization of angular momentum provide calculation procedures that are intimately related. However, different problems require different approaches. If we consider a simple system of a particle moving in a circular orbit (path) about a fixed point, we can show the relation between the wave and angular momentum procedure.

As shown in equation in equation (3.2.5), the wavelength of the wave is related to the mass and velocity of the particle by the expression

$\lambda = h/mv$ ………………………….…. (3.2.6)

As the particle moves in a wavelike manner there is the possibility of both constructive and destructive interferences, in which the waves either cancel out themselves or compliment themselves to become a bigger wave with bigger intensity (Porlie, 1987).

If there is constructive interference the relation between the radius of the orbit and the wavelength is

$2\pi r = n\lambda$ ………………………….... (3.2.7

Where n is an integer which tells the number of waves that fit in the orbit. If we substitute equation (1.5.6) into equation (1.5.7) gives a new relation as

$mvr = nh/2\pi$ ………………………….. (3.2.8)

The LHS of equation (3.2.8) is the angular momentum $I\omega$. By implication, the wave-fitting procedure gives angular momentum restriction.

$I\omega = nh/2\pi$ (n= 1, 2, 3, 4,….) ……………... (3.2.9)

Example

What is the wavelength of a 100eV electron?

Firstly, the speed of the electron must be calculated from the kinetic energy. The relation between the kinetic energy and speed is given as $\text{€} = (½)mv^2$. Therefore, speed is given as

$v = (2\ \text{€}/m)^{½}$

$= [\ (2x100eVx1.602x10^{-19}JeV)/(99.110x10^{-31}kgx1Jkg^{-1}m^{-2}s^{2})]^{½}$

$= 5.930x10^{6}\ ms^{-1}$

On substituting into equation (3.2.6) we obtain

$\lambda = h/mv$

$= (6.626x10^{-34}Js)(10^{9}nm\ m^{-1})/(9.110x10^{-31}kg)(5.930x10^{6}\ ms^{-1})(1Jkg^{-1}m^{-2}s^{2})$

$= 0.12$ nm

This result implies that a 100eV has a wavelength that is within the range of atomic size.

Activity A

(a) define wavefunction;

(b) explain the usefulness of wavefunction;

(c) nature of wavefunction

(d) uncertainty principle

3.4 Application of De Broglie conjecture

The confirmation of the de Broglie conjecture by experiment made it possible to be applied in different electron diffraction of crystalline solids in the same way as X-rays. The diffraction patterns obtained with electron are very similar with those of X-rays. Consequently, the techniques of electron diffraction and neutron diffraction have turned out to be vital tools in the study of molecular structures. This observation implies that the concepts of wave and particle blend together at the atomic level. That is, particles exhibit the properties of waves and waves exhibit those of particles (Porlie, 1987). Similar calculations have led to the results shown in Table 3.2.1.

Table 3.2.1: The de Broglie Wavelength of some typical particles

Particle	Mass (kg)	Velocity (ms^{-1})	Wavelength (nm)
100 eV electron	9.1x10^{-31}	5.9 x10^{6}	0.12
0.025 eV neutron	1.67 x10^{-26}	2.2 x.10^{3}	0.18
H_2 molecule at 200˚C	3.3x10^{-26}	2.4 x 10^{3}	0.080
Galf ball	4.5 x10^{-2}	30	4.9 x10^{-15}

Source: Porlie, (1987). Modern University Chemistry

3.5 Heisenberg's uncertainty principle

Since the electron is described as a wave then its position at a given time cannot be specified with complete accuracy because it is not localised in space. Using electromagnetic radiation of short wavelength we can determine the position and momentum of an electron. The position of the electron cannot be determined more closely than ±λ, where λ is the wavelength of the incident photons. The uncertainty in the position of the electron, Δx, is therefore approximately equal to λ. It has been established above that the momentum of photon of wavelength λ is equal to h/λ. Therefore, the uncertainty in momentum of the electron, $\Delta p = h/\lambda$. The product of the uncertainty in the momentum and position of the electron is

$(\Delta p)(\Delta x) \approx (h/\lambda)(\lambda) \approx h$ …………….. (3.2.10)

This is a simplified statement of Heisenberg's uncertainty principle which indicates that it is impossible to simultaneously measure both the momentum and the position of a particle so that the product of the two uncertainties is less than $h/4\pi$. This is mathematically represented as

$(\Delta p)(\Delta x) \geq h/4\pi$ …………….. (3.2.11)

The implication of the Heisenberg's uncertainty principle is that any effort to minimise the uncertainty in any of the two parameters will definitely lead to increase in the uncertainty of the other such that the relation in equation (3.2.11) is maintained (Porlie, 1987).

Example

An electron travels with the speed of $3x10^{6}$ m s^{-1}.What is the minimum uncertainty in its momentum if we assume that its position is measured within 10% of its atomic radius. Do the same calculation for a 0.03kg ball travelling at a speed of 25 m s^{-1}. Assume that the uncertainty in position of the ball is equal to the wavelength light of 600 nm.

From uncertainty principle the minimum uncertainty in the momentum, (Δp), is

$(\Delta p) = h/4\pi\Delta x$

$= (6.63x10^{-34}Js)/(4\pi)(0.01\ nm)(10^{-9}\ m\ nm^{-1})(1\ Jkg^{-1}m^{-2}s^{2})$

$= 5 \times 10^{-24}$ kg m s^{-1}

The momentum of the electron is $p = mv = (9.1\ x10^{-31})(3x10^{6}\ m\ s^{-1}) = 2.73x\ 10^{-24}$ kg ms^{-1}

The minimum uncertainty is about twice as large as the momentum itself. Such a large uncertainty makes it difficult to predict the position of the particle at a later time.

For the ball, the momentum is $p = (0.03\text{kg})(25\ \text{ms}^{-1}) = 0.75\ \text{kg m s}^{-1}$.

The uncertainty in the momentum of the ball is

$(\Delta p) = h/4\pi\Delta x$

$= (6.63\text{x}10^{-34}\text{Js})/(4\pi)(600\ \text{nm})(10^{-9}\ \text{m nm}^{-1})(1\ \text{Jkg}^{-1}\text{m}^{-2}\text{s}^{2}) = 5.01\ \text{x}10^{-39}\ \text{kg m s}^{-1}$.

This uncertainty in momentum is almost negligible compared to the value of the momentum as to be completely undetectable. The difference between the two cases shows why macroscopic objects behave differently from microscopic ones. This is why the orbits of macroscopic objects like the planets and moon can be calculated to high accuracy and the occurrences of eclipses are predictable even into the far future. On the other hand, as a result of wave nature of microscopic objects, it is impossible to make such predictions about their motion (Porlie, 1987).

Activity B

(a) explain de Broglie conjecture

(b) explain Heisenberg's Uncertainty principle

4.0 Conclusion

The wavefunction is a mathematical function describing the wave.

5.0 Summary

In this unit we have learnt that:

- (i) Once we know the wavefunction of the atom or molecule under study, we can calculate the properties of that atom or molecule.
- (ii) The wave function ψ must obey certain mathematical conditions, that is, ψ(x) be single valued.
- (iii) The wave nature of particles and the quantization of angular momentum provide calculation procedures that are intimately related.
- (iv) The confirmation of the de Broglie conjecture by experiment made it possible to be applied in different electron diffraction of crystalline solids in the same way as X-rays.

6.0 Tutor marked assignment

1. Explain the usefulness of wavefunction.
2. What is the wavelength of a 200eV electron?

7.0 Further reading and references

Barrow, G.M.(1979) Physical Chemistry. McGraw-Hill International. Pp. 79-82.ISBN 0-07-066170-7

Bohr, Niels (1913). "On the Constitution of Atoms and Molecules". *Philosophical Magazine* **26** (1): 476.

Bryson, Bill (2003). *A Short History of Nearly Everything*. Broadway Books. pp. 141-143. ISBN 0-7679-0818-X. Retrieved August 2, 2009 from website: http://en.wikipedia.org/wiki/special:Booksources

Daintith, J. (2004). *Oxford Dictionary of Chemistry*. New York: Oxford University Press. ISBN 0-9-860918-3 http://en.wikipedia.org/wiki/special:Booksources

Griffiths, David (1995). *Introduction to Quantum Mechanics*. Prentice Hall. pp. 190-191. ISBN 0-13-124405-1. Retrieved August 2, 2009 from website: http://en.wikipedia.org/wiki/special:Booksources

Levine, Ira (2000). *Quantum Chemistry* (5 ed.). Prentice Hall. pp. 144-145. ISBN 0-13-685512-1.

Adapted from the Wikipedia article, "Electron_configuration" http://en.wikipedia.org/wiki/Electron_configuration, used under the GNU Free Documentation License

Miessler, Gary L.; Donald A. Tarr (1998). *Inorganic Chemistry (2nd ed.)*. Upper Saddle River, New Jersey: Pearson Education, Inc. Pearson Prentice Hall. ISBN 0138418918.

Mulliken, Robert S. (July 1932). "Electronic Structures of Polyatomic Molecules and Valence. II. General Considerations". *Phys. Rev.* **41** (1): 49-71. Retrieved August 2, 2009 from website: http://prola.aps.org/abstract/PR/v41/i1/p49_1.

Nagaoka, Hantaro (May 1904). "Kinetics of a System of Particles illustrating the Line and the Band Spectrum and the Phenomena of Radioactivity". *Philosophical Magazine* **7**: 445-455. http://www.chemteam.info/Chem-History/Nagaoka-1904.html.

Orchin, M., Macomber, R. S., Pinhas, A. and Wilson, R. M.(2005)"Atomic Orbital Theory" Retrieved August 2, 2009 from website: http://media.wiley.com/product_data/excerpt/81/0471680281.pdf

Porlie, N.T. (1987). Mordern University Chemistry, San Diego, Harcourt Brace Jovanovich

Richard, F. and Sands L. (2006)The Feynman Lectures on Physics -The Definitive Edition, Vol 1 lect 6 pg 11. Addison Wesley ISBN 0-8053-9046-4 Retrieved August 2, 2009 from website: http://en.wikipedia.org/wiki/special:Booksources

Sharma, K,K, and Sharma, L.K. (1977) A Textbook of Physical Chemistry. Vani Educational Books. pp. 547-548. ISBN 0-7069-2833-4

Shannon R.D. (1976) *Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides* Acta Cryst. A32 751-767 doi:10.1107/S0567739476001551

Retrieved August 2, 2009 from website: http://dx.doi.org/10

Module 3: Quantum Mechanics

Unit 3: Particle in a one dimensional (1D) Box

Contents

1.0 Introduction 204

2.0 Objectives 204

3.0 Definition of the particle in a box 205

3.1 The Schrodinger wave Equation 205

3.2 Orthogonal and orthonormal wave funxtions 212

3.3 Free electron model (FEMO) 213

4.0 Conclusion 215

5.0 Summary 215

6.0 Tutor marked assignment 215

7.0 Further reading and references........ 216

1.0 Introduction

The Schrodinger wave equation is of particular interest in Chemistry because it is applicable to behavior of object down to molecular and atomic dimensions. In a study of molecules and atoms, the quantities that must be of prime interest are the energies and the positions of the particles. The Schrodinger method yields the energy directly. It does not give accurate information about the positions of the particles in the system. Only the probability that the particle is at a given position is obtained from wave mechanics. The lack of information about the exact position of a particle at some specific time seems to be a characteristic of the problem rather than a defect in the Schrodinger method.

2.0 Objectives

By the end of this unit, you should be able to;

(a) define particle in a box;

(b) define the terms in the time-independent Schrodinger wave equation;
(c) write the equation for probability of find a particle within the box and
(d) calculate the wave number for transition in a conjugated system.

3.0 Definition of the particle in a box

The simplest system of physical significance is that of a particle constrained to move in a box of given dimension. The particle can be confined to certain region in space by allowing the potential energy to be infinite in any region outside that of interest. If the potential energy is zero within the defined region (that is the box), we have a simple system that still has physical application: translational motion of molecules. The levels can be used in statistical mechanics to calculate energies of molecules. The particle in a box model can also be used to explain the electronic properties of some molecules. We assume that the particle can move in a line only (one-dimensional). The potential outside the box of length "a" is ∞ and obviously $\varphi = 0$ in any region where $V = \infty$. This is because no normal particle will have sufficient energy to exist in the region where $V = \infty$.

3.1 The Schrodinger Wave Equation

In this Unit, we will, for the sake of both brevity and simplicity, only consider the time-independent Schrodinger wave equation in one dimension. We will not consider the full equation in its entire gruesome splendor (Redwoods , 2009). The time-independent Schrodinger wave equation, which could validly be called Schrodinger's law, is given by the differential equation (3.3.1)

$$\frac{d^2\varphi}{dx^2} = -\frac{2m}{\hbar^2}[E - U(x)]\varphi(x)$$

where $\varphi(x)$ is the is the wave function, m is mass, $\hbar$ is Planck's constant divided by 2π, E is the total energy of the particle, and $U(x)$ is the potential energy function of the particle. As when one ingests something disagreeable and the natural reaction is nausea, so too is the natural reaction to this equation. However, comfort may be taken if we consider that acceleration is the second derivative of the position function and, therefore, could be written in the equation (3.3.2).

$$a = \frac{d^2x}{dt^2}$$

As surely as acceleration simplifies to something more palatable, The Schrodinger wave equation must simplify (a little, at least). To find general solutions to this equation, **boundary conditions** must be established. The principle conditions that it must adhere to are

1. $\varphi(x) \to 0$ as $x \to \pm\infty$
2. $\varphi(x) = 0$ if x is in someplace it is physically impossible to be
3. $\varphi(x)$ is a continuous function
4. $\varphi(x)$ is a normalized function

In these pages, we will, again for brevity and simplicity, consider the case of a particle in a one-dimensional box of ideal rigidity, such that its walls are impenetrable. Let the box have length L. As may be seen in the illustration, the potential energy function has two states:

1. $U(x)=0$ for $0 \leq x \leq L$
2. $U(x)=\infty$ for $x<0$ or $x>L$

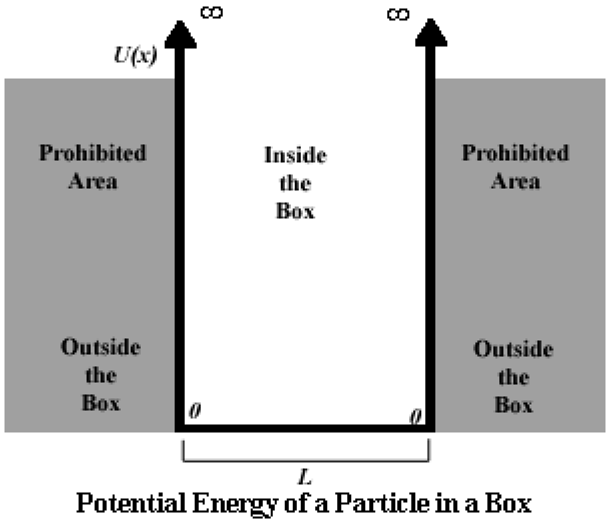


Figure 3.3.1: Potential energy of a particle in a box

Source: http://online.redwoods.cc.ca.us/DEPTS/science/chem

Since it is physically impossible for the particle to be outside of the box, it is the first state that is of interest. Indeed, this simplifies the wave equation considerably, with the term *U(x)* dropping out. Therefore, the wave equation corresponding to the particle in the box is given by equation (3.3.3)

$$\frac{d^2\varphi}{dx^2} = -\frac{2m}{\hbar^2}E\,\varphi(x)$$

Before assailing this equation with a display of mathematical acumen, let us ask ourselves what function's second derivative is merely some negative constant -- all of the terms on the right-hand side save $\varphi(x)$ -- multiple of itself? To simplify, let

$$B^2 = \frac{2mE}{\hbar^2}$$

Therefore, the wave equation (3.3.3) becomes equation (3.3.4)

$$\frac{d^2\varphi}{dx^2} = -B^2\varphi(x)$$

It becomes clear; a trigonometric function like *sine* or *cosine* would be a good candidate for φ *(x)*. Therefore, our guess for the solutions to the wave equations is equation(3.3.5)

$$\varphi(x) = \sin Bx$$

By the first above boundary condition, it is known that

$$\varphi(x = L) = \sin BL = 0$$

Therefore,

$$BL = n\pi \Rightarrow B = \frac{n\pi}{L}$$

where *n*=1,2,3,... When the smoke clears, we have the equation (3.3.6)

$$\varphi(x) = A \sin \frac{n\pi x}{L}$$

where *A* is the function's amplitude. To determine the amplitude, recall the fourth boundary condition, φ *(x)* is a normalized function. Mathematically, this means

In words, this states that the probability of finding the particle somewhere on the x-axis is one or 100%. Waving hands a bit to omit the gory details, this gives equation (3.3.7)

$$A = \sqrt{\frac{2}{L}}$$

Gasping for breath, we at last have unearthed the solution to the wave equation for the particle of the *n*th quantum state in the rigid box we have equation (3.3.8).

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \text{for } 0 \leq x \leq L$$

$$\varphi_n(x) = 0 \quad \text{for } x<0 \text{ or } x>L$$

The utility of this solution lies primarily in that the probability of finding the particle at some position x is given by the square of φ (x) which gives un equation (3.3.9).

$$P_n(x) = |\varphi(x)|^2 = \frac{2}{L} \sin^2 \frac{n\pi x}{L}$$

The importance of this relationship is best illustrated graphically. Consider a particle in the *third* quantum state.

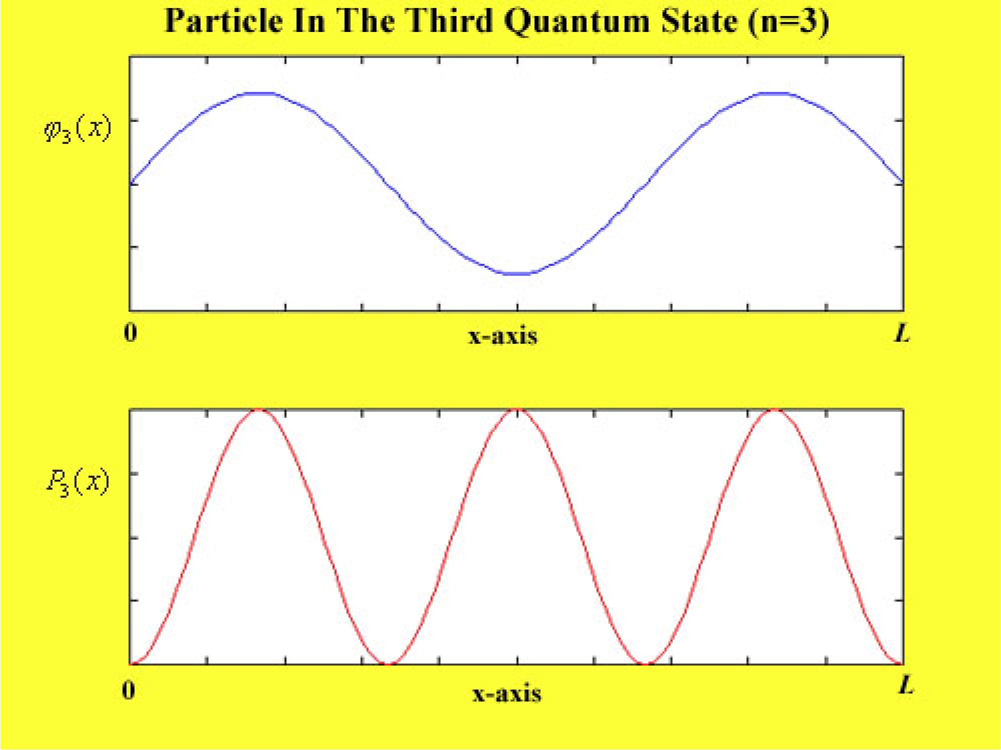


Figure 3.3.2: The third quantum state in a 1D box.

Source: http://online.redwoods.cc.ca.us/DEPTS/science/chem

It can be seen that there are regions where the probability of finding the particle is zero -- so-called **nodes**. This is not unique to simply the particle in a rigid box model. It is observed in more sophisticated ones such as the model of an electron orbiting a nucleus (Redwoods, 2009). This equation can be used to calculate the probability of finding the particle at any point, x. The probability is $[\varphi\ (n,x)]^2$. If the values of n, x and a are known, the probability can be evaluated.

3.2 Orthogonal and orthonormal wave funxtions

Two wave functions are said to be normalized when

$\int_{\infty}^{\infty} \varphi_{i}^{*} * \varphi_{j} d\tau = 1$ if i = j. …………… (3.3.10)

However, $\int_{\infty}^{\infty} \varphi_{i}^{*} \varphi_{j}\, d\tau = 0$ if $i \neq j$. …………………. (3.3.11)

Such wave functions are said to be orthogonal to each other.

The last two expressions can be combined to obtained $\int_{\infty}^{\infty} \varphi_{i}^{*} \varphi_{j}\, d\tau = \sigma_{ij}$ (3.3.12)

Where $\sigma_{ij} = 0$ for $i \neq j$

$\sigma_{ij} = 1$ for $i = j$

Wave functions that satisfy $\int_{\infty}^{\infty} \varphi_{i}^{*} \varphi_{j}\, d\tau = \sigma_{ij}$ …………………. (3.3.13)are said to be orthonormal. Hence wave functions that are normalised and are orthogonal to each other are sometimes called orthonormal functions.

Activity A

(a) define particle in a box.

(b) define the terms in the time-independent Schrodinger wave equation.

(c) write the equation for probability of find a particle within the box.

3.3 Free electron model (FEMO)

The simple calculation done for the particle in a one-dimensional box can be applied to estimate the absorption frequency of some organic molecules presumably conjugated dienes. The method often employed is the free electron model (FEMO) for the Π electrons of these molecules. The energy for the lowest electronic transition is that reqired to raise an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). For molecules with conjugated dienes, it has been found that the electronic absorption bands shift to longer wavelengths as the number of conjugated dienes is increased. Each carbon atom contributes one electron to the Π-system but these electrons are free to move the entire length of the series of Π orbitals and are not localised on a given carbon atom. In FEMO, it is assumed that the Π-system is a region of uniform potential and that the potential energy rises sharply to infinity at the ends of the system. Hence the energy level, E, available to the electrons would be expected to be analogous to that of a particle restricted to move in one dimension. The Π electrons are assigned to orbitals so that there are two in each level (with opposite spin) starting with the lowest. For a completely conjugated system (hydrocarbon), the number of the HOMO is n =N/2 where N is the number Π electrons involved and parallels the number of carbon atoms in the Π system. For absorption, an electron from the HOMO is excited to the LUMO with quantum number n' = (N/2 + 1). The difference in energy between these levels is

$$\Delta E = \frac{h^2}{8ma^2}(n'^2 - n^2) = \frac{h^2}{8ma^2}\{[(N/2) + 1]^2 - (N/2)^2\} \qquad \ldots\ldots\ldots\ldots\ (3.3.14)$$

The absorption frequency in wave numbers is $\Delta E/hc = h(N+1)/8ma^2c$

To estimate ‘a’ two methods are used. Firstly, when end effects are not neglected, ‘a’ equals the sum of bond lengths and half the bond length of extensions at both extremes. Secondly, when end effects are neglected, ‘a’ = 1.54(N + 1) where N is number of carbon atoms in the Π-system.

Example

Calculate the lowest absorption wavenumbers for octatetraene neglecting end effects.

Octatetrene has the csrbon skeleton below.

C=C-C=C-C=C-C=C

Since there are 8 Π electrons in the system (one from each carbon atom) there will be four levels occupied by electrons (in pairs). This means the HOMO is 4 while the LUMO is 5.

Neglecting end effects means that ‘a’ = 1.54(N + 1) = 1.54(8-1) = 10.78Å

$\Delta E = [5^2h^2/8ma^2]- [4^2h^2/8ma^2] = 9h^2/8ma^2$

But $\Delta E = h\nu = 9h^2/8ma^2$

Therefore, wavenumber = $[9x6.626x10^{-34}]/[8x9.11x10^{-31}x(10.78x10^{-10})^2x3x10^8]$

$=2.347x10^6\ m^{-1} = 2.347 \times 10^4\ cm^{-1}$

Activity B

(a) Explain each of the following terms: (1) orthogonal function (2) orthonormal function.

(b) Calculate the wave number for transition in a conjugated system.

4.0 Conclusion

The Schrodinger wave equation is a great tool in Chemistry for understanding the behaviour of object down to molecular and atomic dimensions.

5.0 Summary

In this unit we have learnt that:

- (i) The Schrodinger method yields the energy of the particle directly;
- (ii) The particle in a box model can also be used to explain the electronic properties of some molecules;
- (iii) This equation can be used to calculate the probability of finding the particle at any point, x;
- (iv) The simple calculation done for the particle in a one-dimensional box can be applied to estimate the absorption frequency of some organic molecules presumably conjugated dienes;

6.0 Tutor marked assignment

1. Make a plot of $\varphi\ (n,x)$ and $[\varphi\ (n,x)]^2$ against x for values of $n_x = 1,2,3,4,5,6$ and comment briefly on the shape of your plot.
2. Calculate the lowest absorption wavenumbers for butadiene neglecting end effects.

7.0 Further reading and references

Feynman, R. P. (1994). *Six Easy Peices: The Feynman Lectures on Physics.* New York, New York: Addison-Wesley.

Knight, R. D. (1997). *Physics: A Contemporary Perspective*. Preliminary Edition. New York, New York: Addison-Wesley.

Kotz, J. C. and Vininng, W. J. (1996). *Saunders Interactive Chemistry CD-ROM*. CD-ROM. Harcourt Brace & Co.

Kotz, J. C. and Treichel, P. (1996). *Chemistry and Chemical Reactivity*. Third Edition. Harcourt Brace & Co.

Redwoods (2009). Adapted August 2,2009 from wesite: http://online.redwoods.cc.ca.us/DEPTS/science/chem

Tipler, P. (1991).*Physics for Scientists and Engineers Volume II*. Third Edition. New York, New York: Worth Publishing.

Module 3: Quantum mechanics

Unit 4: Particle in a Three-Dimensional (3D) Box

Contents

1.0 Introduction 218

2.0 Objectives........ 218

3.0 Definition of Particle in a three-Dimensional Box 219

4.0 Conclusion........ 224

5.0 Summary 224

6.0 Tutor marked assignment 225

7.0 Further reading and references........ 225

1.0 Introduction

Suppose we consider the same particle as in Unit 3 but that this time that it is constrained to move in a rectangular box of dimensions a, b and c in length. Within the box (i.e. between x= 0 and a; y = 0 and b and z = 0 and c), the potential energy is zero. At the walls and everywhere outside the box, the potential is ∞.

2.0 Objectives

By the end of this unit, you should be able to:

(a) write equation for the 3D Schrodinger wave equation;
(b) draw the diagram for the quantized energy levels of a particle in a 3D and
(c) calculate the energy difference when there is transition between two energy levels.

3.0 Definition of Particle in a three-Dimensional Box

The Schrodinger wave equation for 3 dimensional (3D) box is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\,\psi = 0 \qquad \ldots\ldots\ldots\ldots (3.4.1)$$

where ψ and V are f(x,y,z).

since V = 0 inside the box, then the equation (3.4.1) becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}E\psi = 0 \qquad \ldots\ldots\ldots\ldots (3.4.2)$$

Equation (3.4.2) may be solved by writing the wave function as the product of three functions, each depending on one coordinate.

$$\psi\,(x, y, z) = X(x)Y(y)Z(z) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.4.3)$$

differentiating equation (3.3.3) gives

$$\frac{\partial\psi}{\partial x} = Y\,(y)\;Z\,(z)\,\frac{\partial x}{\partial x}$$

$$\frac{\partial^2\psi}{\partial x^2} = Y\,(y)\;Z(z)\,\frac{\partial^2 x}{\partial x^2} \qquad \ldots\ldots\ldots (3.4.4a)$$

and by a similar reasoning

$$\frac{\partial^2\psi}{\partial y^2} = X\,(x)\;Z(z)\,\frac{\partial^2 y}{\partial y^2} \qquad \ldots\ldots\ldots\ldots (3.4.4b)$$

$\frac{\partial^2 \psi}{\partial z^2}$ = X (x) Y(y) $\frac{\partial^2 z}{\partial z^2}$ ……….. (3.4.4c)

substituting equations (3.4.4a), (3.4.4b) and (3.4.4c) into equation (3.4.2) gives

Y(y)Z(z) $\frac{\partial^2 x}{\partial x^2}$ + X(x)Z(z)$\frac{\partial^2 y}{\partial y^2}$ + X(x)Y(y) $\frac{\partial^2 z}{\partial z^2}$ +$\frac{8\pi^2 m}{h^2}$ EX(x)Y(y)Z(z) = 0 …. (3.4.5)

dividing all through by Y(y)X(x)Z(z) one obtains

$$-\frac{h^2}{8\pi^2 m}\frac{1}{X(x)}\frac{\partial^2 x}{\partial x^2} + \frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)}\frac{\partial^2 Z(z)}{\partial z^2} = E \quad \ldots\ldots \quad (3.4.6)$$

we can write the energy as the sum of three contributions associated with the coordinates.

E = $E_x + E_y + E_z$ ……….. (3.4.7using equation (3.4.7), we can separate the expression obtained into three equations.

$$-\frac{h^2}{8\pi^2 m}\frac{1}{X}\frac{\partial^2 x}{\partial x^2} = E_x \quad \ldots\ldots \quad (3.4.8)$$

$$-\frac{h^2}{8\pi^2 m}\frac{1}{Y}\frac{\partial^2 y}{\partial y^2} = E_y \quad \ldots\ldots. \quad (3.4.9)$$

$$-\frac{h^2}{8\pi^2 m}\frac{1}{Z}\frac{\partial^2 z}{\partial z^2} = E_z \quad \ldots\ldots\ldots\ldots \quad (3.4.10)$$

Each of the last three equations is similar to the expression for the particle in a one-dimensional box discussed in Unit 3. Hence their solutions are respectively;

X = [√(2/a)]sin $\frac{n\pi x}{a}$ ……….. (3.4.11)

$$E_{n,x} = \frac{n_x^2 h^2}{8ma^2} \qquad \ldots\ldots\ldots\ldots \quad (3.4.12)$$

$$Y = [\sqrt{(^2/b)}]\,\sin\frac{n\pi y}{b} \qquad \ldots\ldots\ldots\ldots.. \quad (3.4.13)$$

$$E_{n,y} = \frac{n_y^2 h^2}{8mb^2} \qquad \ldots\ldots\ldots.. \quad (3.4.14)$$

$$X = [\sqrt{(^2/c)}]\,\sin\frac{n\pi x}{c} \qquad \ldots\ldots\ldots \quad (3.4.15)$$

$$E_{n,z} = \frac{n_z^2 h^2}{8mc^2} \qquad \ldots\ldots\ldots\ldots. \quad (3.4.16)$$

Where a, b, c are length in x, y, z directions, respectively. Also, n_x, n_y, n_z are the quantum numbers respectively.

Since ψ (x, y, z) = X(x)Y(y)Z(z) and $E = E_x + E_y + E_z$, then

$$\psi\,(x,y,z) = \sqrt{\frac{8}{v}}\,\sin(\frac{n\pi x}{a})\sin(\frac{n\pi y}{b})\sin(\frac{n\pi z}{c}) \qquad \ldots\ldots\ldots\ldots\ldots. \quad (3.4.17)$$

where V is the volume of the box.

$$E_{x,y,z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad \ldots\ldots\ldots\ldots\ldots. \quad (3.4.18)$$

Whenever the 3 dimensional box has geometrical symmetry, more interesting results are often obtained. For example, in a cubic box, a = b =c, thus equation (3.4.18) becomes

$$E = \frac{h^2}{8m} \; (n_x^2 + n_y^2 + n_z^2) \qquad \ldots\ldots\ldots\ldots \; (3.4.19)$$

Suppose $n_x = 3$, $n_y = n_z = 2$, then

$$\Psi(x,y,z) = [\sqrt{(\tfrac{8}{v})}]\sin\frac{3\pi x}{a}\sin\frac{2\pi y}{a}\sin\frac{2\pi z}{a} \qquad \ldots\ldots\ldots\ldots\ldots (3.4.20)$$

$$E = \frac{h^2}{8ma^2}\,(3^2 + 2^2 + 2^2) = \frac{17h^2}{8ma^2} \qquad \ldots\ldots\ldots\ldots \; (3.4.21)$$

Assuming we have another set of values $n_x = 2$, $n_y = 3$, $n_z = 2$, then

$$\Psi(x,y,z) = [\sqrt{(\tfrac{8}{v})}]\sin\frac{2\pi x}{a}\sin\frac{3\pi y}{a}\sin\frac{2\pi z}{a} \qquad \ldots\ldots\ldots (3.4.22)$$

$$E = \frac{h^2}{8ma^2}\,(2^2 + 3^2 + 2^2) = \frac{17h^2}{8ma^2} \qquad \ldots\ldots\ldots\ldots\ldots \; (3.4.23)$$

Suppose $n_x = 2$, $n_y = 2$, $n_z = 3$, then

$$\Psi(x,y,z) = [\sqrt{(\tfrac{8}{v})}]\sin\frac{2\pi x}{a}\sin\frac{2\pi y}{a}\sin\frac{3\pi z}{a} \qquad \ldots\ldots\ldots (3.4.24)$$

$$E = \frac{h^2}{8ma^2}\,(2^2 + 2^2 + 3^2) = \frac{17h^2}{8ma^2} \qquad \ldots\ldots\ldots (3.4.25)$$

Even though these states are different, the values of the energies [as in equations (3.4.21), (3.4.23), (3.4.25)] are the same. The three states are said to be degenerate because they have equal energy.

For a situation where $n_x = n_y = n_z = 1$, it corresponds to only one state of the system. The same is true of $n_x = n_y = n_z = 2$, but situations such as $n_x \neq n_y = n_z$ three degenerate states are obtained as shown in the Figure below.

Activity A

(a) Write equation for the 3D Schrodinger wave equation and explain each of the terms.

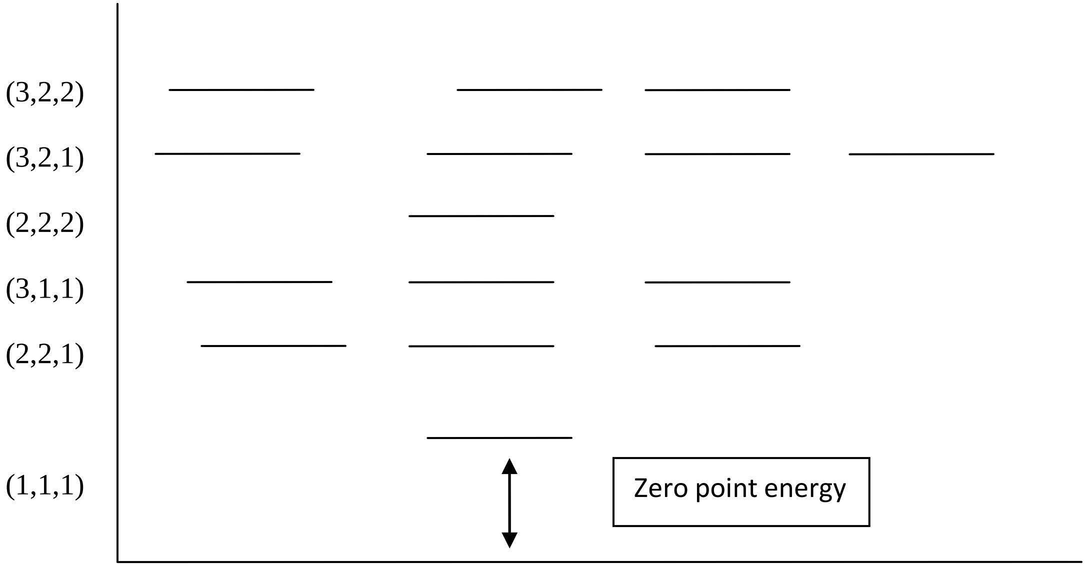


Figure 3.4.1: Quantized energy levels of a particle in a cubic box.

Suppose we wish to calculate the transition energy between the levels $E_{2,2.2}$ and $E_{3,2,1}$ then the energy difference is calculated as

$$\Delta E = h\nu = \frac{14h^2}{8ma^2} - \frac{12h^2}{8ma^2} = \frac{2h^2}{8ma^2} = \frac{h^2}{4ma^2}$$

Given appropriate data, it should be possible for us to evaluate the frequency (ν) of the transition between the two states.

Zero point energy

According the old quantum theory, the energy level of a harmonic oscillator is $E = h\nu$.

The lowest energy level with $n = 0$ would have zero energy. Based on the wave treatment of the system, the energy level corresponds to the state with quantum numbers $n_x = n_y = n_z = 1$. The difference between these two values is called the zero point energy.

Activity A

(a) Calculate the energy difference between the (3,2,1) and the (2,2,2) states.

(b) Calculate the frequency of transitions between the two states above in terms of the unknown parameters.

4.0 Conclusion

The 3D Schrodinger equation may be solved by writing the wave function as the product of three functions, each depending on one coordinate.

5.0 Summary

In this unit, we have learnt that;

(i) For a 3D box the potential energy is zero within the box but at the walls and everywhere outside the box, the potential is ∞.

(ii) Whenever the 3 dimensional box has geometrical symmetry, more interesting results are often obtained.

(iii) The zero point energy is the energy difference between lowest energy level with n = 0 and that at which $n_x = n_y = n_z = 1$.

6.0 Tutor marked assignment

1. write equation for the 3D Schrodinger wave equation;
2. draw the diagram for the quantized energy levels of a particle in a 3D and
3. calculate the energy difference when there is transition between two energy levels.

7.0 Further reading and references

Atkins, P. W. (1982). Physical Chemistry, (2_{nd} ed.), Oxford, Oxford University Press.

Landau, L.D. and Lifshitz, E.M. *Quantum Mechanics:Non-relativistic Theory* (Course of Theoretical Physics vol.3) (Pergamon Press)

McWeeny, R. *Coulson's Valence* (Oxford Science Publications) ISBN 0-19-855144-4

Pauling, L. (1954). *General Chemistry*. Dover Publications. ISBN 0-486-65622-5.

Pauling, L., and Wilson, E. B. *Introduction to Quantum Mechanics with Applications to Chemistry* (Dover Publications) ISBN 0-486-64871-0

Pullman, B. and Pullman, A. (1963). *Quantum Biochemistry.*, New York and London: Academic Press.

Module 3: Quantum mechanics

Unit 5: Application of Schrodinger wave equation to bonding in molecules

Contents

1.0 Introduction....227

2.0 Objectives....227

3.0 Definition bond formation in molecules....228

  3.1 The wavefunction....228

  3.2 Quantum mechanics of atoms....229

  3.3 Quantum mechanics of molecules....229

  3.4 The hydrogen molecule ion....230

  3.5 The hydrogen molecule....233

  3.6 Variation method....237

4.0 Conclusion 239

5.0 Summary...239

6.0 Tutor marked assignment **…...……………………………………………………………… 12**

7.0 Further reading and references..240

1.0 Introduction

Chemical bonding involves two or more atoms coming together due to the force of interaction between them. The aggregate molecule that is formed has lower energy than the separated fragments and when this energy lowering exceeds 41.8 kJ mol^{-1}of atoms, we say that a chemical bond exists.

2.0 Objectives

By the end of this unit, you should be able to;

(a) state the conditions for the formation of chemical bond

(b) write the Schrodinger wave equation for the hydrogen molecule ion;

(c) write the Schrodinger wave equation for the hydrogen molecule and

(d) draw the potential energy curve for a diatomic molecule.

3.0 Definition of bond formation in molecules

If we consider two atoms A and B separated by some distance r. Depending on the magnitude of r, there is bound to be attraction or repulsion. If the attractive force is greater than the repulsive force, the net effect is a chemical bond being formed whereas the converse is also true.

3.1 The Wavefunction

For a scientist, knowing that matter behaves as a wave is useful only if one knows something about that wave. The wavefunction is a mathematical function describing the wave. For example, $y(x) = A \sin(kx)$ might be the wave-function for a one-dimensional wave, which exists along the x-axis. Matter waves are three-dimensional; the relevant wavefunction depends on the $x, y,$ and z coordinates of the system being studied (and sometimes on time as well). We conventionally label the wavefunction for a three-dimensional object as $\psi(x, y, z)$. In 1926 Erwin Schrödinger introduced a mathematical equation whereby, if one knows the potential energy acting on an object, one can calculate the wavefunction for that object. Heisenberg had already introduced a mathematical formalism for performing quantum mechanics calculations, without explicitly including the concept of waves. It was later shown that, although the approaches of Schrödinger and Heisenberg looked very different, they made exactly the same predictions. In practice, the Schrödinger formalism is more useful for explaining the problem being studied, and the Heisenberg methodology allows for more straightforward computation. Accordingly, a mixture of the two approaches is typically used in modern quantum chemistry. Once we know the wavefunction of the atom or molecule under study, we can calculate the properties of that atom or molecule.

3.2 Quantum Mechanics of Atoms

An exact solution for Schrödinger's wave equation can be obtained for the hydrogen atom; however, for larger atoms and molecules (which contain more than one electron), Schrödinger's equation can be solved only approximately. Although this may sound so restrictive as to make the equation useless, there are well-established approaches that allow for practical and accurate calculations on atoms and molecules. This is done by making some assumptions about larger systems based upon the hydrogen atom, as explained below.

When the Schrödinger equation is solved for the hydrogen atom, the resulting wavefunctions for the various possible energies that the atom can have are used to determine **atomic orbitals**. An orbital is a region in space where an electron is most likely to be found. For example, the lowest-energy wavefunction for a hydrogen atom is the so-called 1s orbital, which is a spherical region in space surrounding the nucleus. For some higher-energy states, the orbitals are not necessarily spherical in shape (e.g., the 2p orbital).

For atoms larger than hydrogen, one assumes that the orbitals occupied by the electrons have the same shape as the hydrogen orbitals but are differing in size and energy. The energies corresponding to these orbitals may be found by solving an approximate version of Schrödinger's equation. These atomic orbitals, in turn, may be used as the building blocks to the electronic behavior in molecules, as we shall see below. As it happens, two electrons may share an atomic orbital; we say that these electrons are paired. Chemists have developed a system of rules for determining which orbitals are occupied in which atoms; calculations can then be done to determine the energies of the electrons in the atoms.

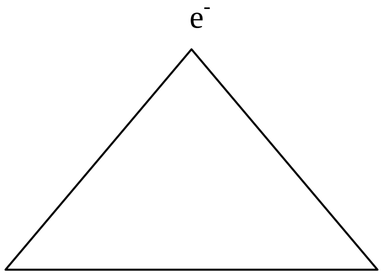
3.3 Quantum mechanics of molecules

Molecules are held together by **covalent bonds**. The simplest definition of a covalent bond is a shared pair of electrons. There are two basic approaches to modeling covalent bonds in molecules: the **valence** bond model and the molecular orbital model. In the valence bond model, we think of atomic orbitals on each of two atoms combining to form a bond orbital, with one electron from each atom occupying this orbital. Both the bond orbital and the electron pair now "belong" to both of the atoms. This sharing of electrons brings about a lowering in the energy, which makes the formation of molecules from atoms an energetically favorable process. The valence bond model gives the simplest quantum mechanical picture of chemical bonding, but it is not the best method for accurate calculations on molecules containing more than two atoms.

Molecular orbital theory differs from valence bond theory in that it does not require the electrons involved in a bond to be localized between two of the atoms in a molecule. Instead, the electron occupies a molecular orbital, which may be spread out over the entire molecule. As in the valence bond approach, the molecular orbital is formed by adding up contributions from the atomic orbitals on the atoms that make up the molecule. This approach, which does not explicitly model bonds as existing between two atoms, is somewhat less appealing to the intuition than the valence bond approach. However, molecular orbital calculations typically yield better predictions of molecular structure and properties than valence bond methods. Accordingly, most commercially available quantum chemistry software packages rely on molecular orbital methods to perform calculations.

3.4 The hydrogen molecule ion

The hydrogen molecule ion consists of 2 protons and 1 electron. It is therefore the simplest molecular system that can be encountered in nature. The molecule ion is often represented as



The hydrogen molecule ion is represented by the triangle above. The two hydrogen atoms are represented by A and B while the only electron is represented by e-. The distance between A and B is the internuclear distance r_{AB} while the distance between the electron and each of the atoms refers to the sides of the triangle, r_A and r_B, respectively.

The interactions among the species are as follow:

1. Attractive interaction between the electron and nucleus A;
2. Attractive interaction between the electron and nucleus B;
3. Repulsive interaction between the two nuclei.

The potential energy (U) for the hydrogen molecule ion is

$$U = -\frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{r_{AB}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.5.1)$$

The first two terms in equation (3.5.1) represent the electrostatic attraction between the nuclei and the electron while the last term represents the repulsion between the nuclei. The kinetic energy (K.E.) for the molecule is

$$K.E = \frac{P^2}{2m} = \frac{I}{2m}(p_x^2 + p_y^2 + p_z^2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.5.2)$$

Where p= momentum of the electron,

m = mass of the electron

The electron is assumed to be moving in the three directions in space. It should be noted that we have assumed r_{AB} fixed, which implies that only one K.E. term needs to be considered; the K.E. due to the electron motion. The 3D Schrodinger equation is

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} + \frac{8\pi^2 m}{h^2}[E- U)(x,y,z)]\, \psi = 0 \qquad \ldots\ldots \ (3.5.3)$$

Which can be written as

$$H\varphi = E\varphi \qquad \ldots\ldots\ldots \ (3.5.4)$$

$$\text{Where } H = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U\,(x,y,z) \qquad \ldots\ldots.. \ (3.5.5)$$

Known as the Hamiltonian operator and

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \ldots\ldots\ldots\ldots \ (3.5.5)$$

is a Laplacian operator.

Equation (3.5.4) is known as the Hamiltonian form of Schrodinger equation.

It should also be noted that

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(x,y,z) \qquad \ldots. \quad (3.5.6)$$

The Schrodinger equation for the hydrogen molecule ion is

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + \frac{e^2}{r_{AB}} - \frac{e^2}{r_A} - \frac{e^2}{r_B}\right)\psi + E\,\psi \qquad \ldots\ldots\ldots.. \quad (3.5.7)$$

This wave equation is simple and it is possible to get an exact solution for it.

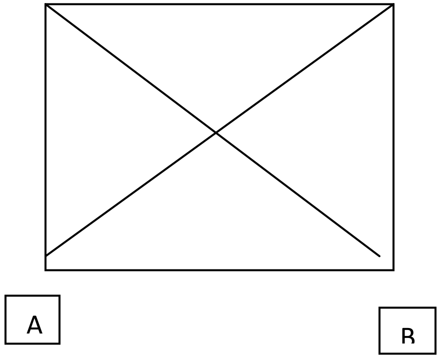
Activity A

(a) State the conditions for the formation of chemical bond

(b) Write the Schrodinger wave equation for the hydrogen molecule ion;

3.5 The hydrogen molecule

The hydrogen molecule has two electrons (e_1 and e_2) and two nuclei (A and B). The coordinate in the hydrogen molecule is as shown below.



The interactions among the species are as follow:

4. Repulsive interaction between the two electrons;

5. Attractive interaction between the first electron and nucleus A;

6. Attractive interaction between the first electron and nucleus B;

7. Attractive interaction between the second electron and nucleus A;

8. Attractive interaction between the second electron and nucleus B;

9. Repulsive interaction between the two nuclei.

The steps involves in writing the Schrodinger equation for this molecule are:

1. Writing the expression for the K.E.;

2. Writing expression for the P.E.;

3. Inserting the two expression above in the Schrodinger equation.

Total K.E. for the system = (K.E.)$_1$+(K.E.)$_2$ =

$$\text{K.E.} = \frac{P_1^2}{2m} + \frac{P_2^2}{2m} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.5.8)$$

Where 1, 2 stand for the first and second electrons, respectively.

$$\text{Total K.E} = \frac{I}{2m}\left(P_{x1}^2 + P_{y1}^2 + P_{z1}^2\right) + \frac{I}{2m}\left(P_{x2}^2 + P_{y2}^2 + P_{z2}^2\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.5.9)$$

$$U(x,y,z) = -\frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{AB}} + \frac{e^2}{r_{12}} \quad \ldots\ldots\ldots\ldots \quad (3.5.10)$$

The Schrodinger equation for the hydrogen molecule is

$$\left(-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{AB}} + \frac{e^2}{r_{12}}\right)\psi = E\psi \qquad (3.5.11)$$

which transforms to

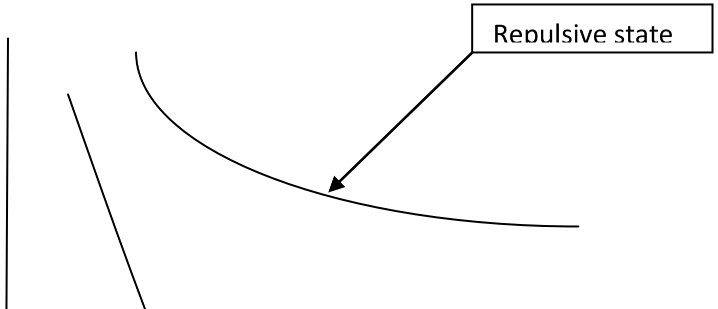
$$\left(\nabla_1^2 + \nabla_2^2\right)\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r_{1A}} + \frac{e^2}{r_{1B}} + \frac{e^2}{r_{2A}} + \frac{e^2}{r_{2B}} - \frac{e^2}{r_{AB}} - \frac{e^2}{r_{12}}\right)\psi = 0 \qquad (3.5.12)$$

This is the required equation.

Whereas it is possible to get an exact solution to Schrodinger equation for hydrogen molecule ion, by separating into any other coordinates (e.g. polar coordinates), we cannot solve the equation for the hydrogen molecule because of the presence of repulsive term (e^2/r_{12}). In this situation, we use an approximate method to get the solution to the Schrodinger equation. We always aim at the energy of the system in joint form compared with when the atoms are far apart. We have assumed that both nuclei A and B are fixed meaning that their K.E. will be almost zero. Thus instead of the

$$K.\ E. = (K.E.)_A + (K.E)_B + (K.E.)_1 + (K.E.)_2 \qquad (3.5.13)$$

We have neglected that due to the nucleus in both equations for hydrogen molecule above. The justification for doing this is that the motions of nuclei in ordinary molecular vibrations are so slow compared to the motions of the electrons that it is possible to calculate the electronic states on assumption that the nuclei are held in fixed position. This is the Born-Oppenheimer approximation. What this means is that in equation for hydrogen molecule for instance, we consider r_{AB} constant. We can therefore calculate E for this fixed value of r_{AB}. If we change the value of r_{AB}, a corresponding value of $E(r_{AB})$ can be got. Thus it should be possible to make a plot of $E(r_{AB})$ against r_{AB} as shown in the Figure below **(Figure 3.5.1)** which is known as the potential energy curve. In the Figure, the equilibrium inter nuclear distance is r_{eq} and corresponds to the region where the total energy of the system is a minimum (that is the system is stable there). It is called the bond length. When r is small, the molecule is unstable due to high repulsive force and also whenever r is large, it is unstable due low attractive force which may not be large enough to offset the repulsive force. In between position A and B, in the Figure the molecule is stable but is not stable at r_{eq}.



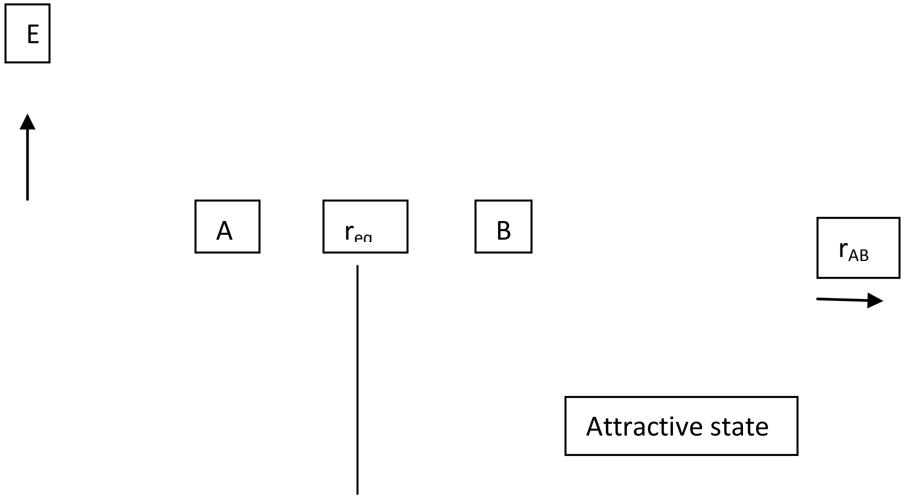


Figure 3.5.1: Potential energy curve showing the variation of the total energy of the system with the internuclear distance r_{AB}.

We cannot obtain exact value of E for the hydrogen molecule because of the presence of the repulsive term which made it impossible for us to separate the molecule into hydrogen atoms for which two electrons are involved. Also the presence of n_1^2 and n_2^2 in the Schrodinger equation for the hydrogen molecule suggests that we should look for another way of solving the equation. The approximate method known as the variation method is often employed.

3.6 Variation Method

It is an approximate method for solving the Schrodinger equation as in equation (3.4.12) since an exact solution of it is not possible. The Schrodinger equation in Hamiltonian form is $H\psi = E\,\psi$.

Multiplying both sides by ψ^* and integrating over all space to get

$$\int \psi^* H \psi \, d\tau = \int \psi^* E' \psi \, d\tau \qquad \text{………..(3.5.14)}$$

$$\text{Therefore } E' = \frac{\int \psi^* H \Psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad \text{…………. (3.5.15)}$$

where E’ indicates the energy that results from an inexact wave function and H is the complete Hamiltonian for the system. Note that E’ is constant. Equation (3.5.15) gives a true value for E’ if ψ is the exact wave function. However, ψ is only an approximation hence the value of E’ will will not be true value. In essence, we want to obtain an approximation value for E’ for which acceptable wave function exists. The latter will be acceptable if finite and single valued. It must also be continuous and its first and second derivatives must be continuous as well. It should be possible to normalize the function.

In molecular terms, we don’t know ψ, so we guess at a function, ψ_1. From this we can calculate a corresponding value for E’. We can also guess at ψ_2 and hence deduce E_1’. We can also guess at ψ_2 and hence E_2’ an so on. The variation theorem states that out of the E_1’, E_2’, , …. En’, one will be the smallest and that if the true energy of the system is E, the lowest calculated value of E_i’ (i= 1,2,3,4,,,) is not smaller than the true energy of the system. That is $E' \geq E_{true}$.

Since the true energy of the system is the minimum energy from the potential energy curve, E' will represent the smallest eigen value calculated. If you have ψ_1, ψ_2 and ψ_3, instead of doing the calculation three times, we get a linear combination of these and feed the result into equation (3.5.15). Thus $\psi = c_1\psi_1 + c_2 \psi_2 + c_3\psi_3$

Ψ is a master wve function and c_1, c_2, c_3 are known as the variation parameters. We shall then obtain the energy E' in terms of c_1, c_2, c_3, which we can minimize. The result obtained will be found to be greater than or equal to the true energy of the system.

Activity B

State the forces that are present in each of the following: (a) Hydrogen molecule ion (b) Hydrogen molecule.

4.0 Conclusion

The success of wave-particle duality in describing the properties of light paved the way for using that same idea in describing matter.

5.0 Summary

In this unit we have learnt that:

(i) A molecule is formed when it has lower energy than the separated fragments and when this energy lowering exceeds 41.8 kJ mol^{-1} of atoms, we say that a chemical bond exists.

(ii) If the attractive force between the electron and the nuclei is greater than the repulsive force between the nuclei, the net effect is a chemical bond being formed whereas the converse is also true.

(iii)The bond length is the equilibrium inter nuclear distance ,r_{eq}, and corresponds to the region where the total energy of the system is a minimum (that is the system is stable there).

6.0 Tutor marked assignment

1. state the condition for the formation of chemical bond;
2. write the Schrodinger wave equation for the hydrogen molecule ion;
3. write the Schrodinger wave equation for the hydrogen molecule and
4. draw the potential energy curve for a diatomic molecule.

7.0 Further reading and references

Atkins, P. W. (1982). Physical Chemistry, (2_{nd} ed.), Oxford, Oxford University Press.

Landau, L.D. and Lifshitz, E.M. *Quantum Mechanics:Non-relativistic Theory* (Course of Theoretical Physics vol.3) (Pergamon Press)

McWeeny, R. *Coulson's Valence* (Oxford Science Publications) ISBN 0-19-855144-4

Pauling, L. (1954). *General Chemistry*. Dover Publications. ISBN 0-486-65622-5.

Pauling, L., and Wilson, E. B. *Introduction to Quantum Mechanics with Applications to Chemistry* (Dover Publications) ISBN 0-486-64871-0

Pullman, B. and Pullman, A.(1963). *Quantum Biochemistry.*, New York and London: Academic Press.

`Module 4: Theory of molecular spectroscopy

Unit 1: Rotational spectroscopy

Contents

1.0 ntroduction 243

2.0 Objectives 243

3.0 Definition of rotational spectroscopy **2**

3.2 Understanding the rotational spectrum 245

3.3 Classification of molecules based on rotational behavior 245

3.4 Structure of rotational spectrum 248

3.5 Hyperfine interactions 254

3.6 Experimental determination of the spectrum 255

3.7 Applications 257

4.0 Conclusion 258

5.0 Summary 258

6.0 Tutor marked assignment 258

7.0 Further reading and references 259

1.0 Introduction

Atoms, ions, and molecules emit or absorb characteristically; only certain energies of these species are possible; the energy of the photon (quantum of radiant energy) emitted or absorbed corresponds to the difference between two permitted values of the energy of the species, or energy levels. (If the flux of photons incident upon the species is great enough, simultaneous absorption of two or more photons may occur.) Thus the energy levels may be studied by observing the differences between them. The absorption of radiant energy is accompanied by the promotion of the species from a lower to a higher energy level; the emission of radiant energy is accompanied by falling from a higher to a lower state; and if both processes occur together, the condition is called resonance.

2.0 Objectives

By the end of this Unit, you should be able to:

(a) define what spectroscopy is;
(b) explain the theory of rotational spectroscopy;
(c) draw energy diagram for rotational spectroscopy;
(d) use rotational spectroscopy to determine the structures of small molecules and
(e) classify molecules based on rotational behavior.

3.0 Definition of Rotational Spectroscopy

Rotational spectroscopy or microwave spectroscopy studies the absorption and emission of electromagnetic radiation (typically in the microwave region of the electromagnetic spectrum) by molecules associated with a corresponding change in the rotational quantum number of the molecule (Wikipedia, 2009).

3.1 Principle of rotational spectroscopy

The use of microwaves in spectroscopy essentially became possible due to the development of microwave technology for RADAR during World War II. Rotational spectroscopy is only really practical in the gas phase where the rotational motion is quantized. In solids or liquids the rotational motion is usually quenched due to collisions.

Rotational spectrum from a molecule (to first order) requires that the molecule have a dipole moment and that there is a difference between its center of charge and its center of mass, or equivalently a separation between two unlike charges. It is this dipole moment that enables the electric field of the light (microwave) to exert a torque on the molecule causing it to rotate more quickly (in excitation) or slowly (in de-excitation). Diatomic molecules such as dioxygen (O_2), dihydrogen (H_2), etc. do not have a dipole moment and hence no purely rotational spectrum. However, electronic excitations can lead to asymmetric charge distributions and thus provide a net dipole moment to the molecule. Under such circumstances, these molecules will exhibit a rotational spectrum (Wikipedia, 2009).

Amongst the diatomic molecules, carbon monoxide (CO) has one of the simplest rotational spectra. As for tri-atomic molecules, hydrogen cyanide ($HC{\equiv}N$) has a simple rotational spectrum for a linear molecule and hydrogen isocyanide ($HN{=}C{:}$) for a non-linear molecule. As the number of atoms increases the spectrum becomes more complex as lines due to different transitions start overlapping.

3.2 Understanding the rotational spectrum

In quantum mechanics the free rotation of a molecule is quantized, that is the rotational energy and the angular momentum can only take certain fixed values; what these values are is simply related to the moment of inertia, I, of the molecule. In general for any molecule, there are three moments of inertia: I_A, I_B and I_C about three mutually orthogonal axes A, B, and C with the origin at the center of mass of the system. A linear molecule is a special case in this regard. These molecules are cylindrically symmetric and one of the moment of inertia (I_A, which is the moment of inertia for a rotation taking place along the axis of the molecule) is negligible (i.e. $I_A \ll I_B = I_C$).

3.3 Classification of molecules based on rotational behavior

The general convention is to define the axes such that the axis A has the smallest moment of inertia (and hence the highest rotational frequency) and other axes such that $I_A \leq I_B \leq I_C$. Sometimes the axis A may be associated with the symmetric axis of the molecule, if any. If such is the case, then I_A need not be the smallest moment of inertia. To avoid confusion, we will stick with the former convention for the rest of the article (Wikipedia, 2009). The particular pattern of energy levels (and hence of transitions in the rotational spectrum) for a molecule is determined by its symmetry. A convenient way to look at the molecules is to divide them into four different classes (based on the symmetry of their structure). These are,

1. Linear molecules (or linear rotors)
2. Symmetric tops (or symmetric rotors)
3. Spherical tops (or spherical rotors) and
4. Asymmetric tops

Dealing with each in turn:

1. *Linear molecules:*
   - As mentioned earlier, for a linear molecule $I_A \ll I_B = I_C$. For most of the purposes, I_A is taken to be zero. For a linear molecule, the separation of lines in the rotational spectrum can be related directly to the moment of inertia of the molecule, and for a molecule of known atomic masses, can be used to determine the bond lengths (structure) directly. For diatomic molecules this process is trivial, and can be made from a single measurement of the rotational spectrum. For linear molecules with more atoms, rather more work is required, and it is necessary to measure molecules in which more than one isotope of each atom have been substituted (effectively this gives rise to a set of simultaneous equations which can be solved for the bond lengths).
   - Examples or linear molecules: dioxygen (O=O), carbon monoxide ($O\equiv C^*$), hydroxy radical (OH), carbon dioxide (O=C=O), hydrogen cyanide ($HC\equiv N$), carbonyl sulfide (O=C=S), chloroethyne ($HC\equiv CCl$), acetylene ($HC\equiv CH$)
2. *Symmetric tops:*
   - A symmetric top is a molecule in which two moments of inertia are the same. As a matter of historical convenience, spectroscopists divide molecules into two classes of symmetric tops, *Oblate symmetric tops* (saucer or disc shaped) with $I_A = I_B <$

I_C and *Prolate symmetric tops* (rugby football, or cigar shaped) with $I_A < I_B = I_C$. The spectra look rather different, and are instantly recognizable. As for linear molecules, the structure of *symmetric tops* (bond lengths and bond angles) can be deduced from their spectra.

- Examples of symmetric tops:
  - Oblate: benzene (C_6H_6), cyclobutadiene (C_4H_4), ammonia (NH_3)
  - Prolate: chloromethane (CH_3Cl), propyne ($CH_3C{\equiv}CH$)

3. *Spherical tops:*

- A spherical top molecule, can be considered as a special case of *symmetric tops* with equal moment of inertia about all three axes ($I_A = I_B = I_C$).
- Examples of spherical tops: phosphorus tetramer (P_4), carbon tetrachloride (CCl_4), nitrogen tetrahydride (NH_4), ammonium ion (NH_4^+), sulfur hexafluoride (SF_6)

4. *Asymmetric tops:*

- As you would have guessed a molecule is termed an asymmetric top if all three moments of inertia are different. Most of the larger molecules are asymmetric tops, even when they have a high degree of symmetry. Generally for such molecules a simple interpretation of the spectrum is not normally possible. Sometimes asymmetric tops have spectra that are similar to those of a linear molecule or a symmetric top, in which case the molecular structure must also be similar to that of a linear molecule or a symmetric top. For the most general case, however, all that can be done is to fit the spectra to three different moments of inertia. If the molecular formula is known, then educated guesses can be made of the possible structure, and from this guessed structure, the moments of inertia can be calculated. If the calculated moments of inertia agree well with the measured moments of inertia, then the structure can be said to have been determined. For this approach to determining molecular structure, isotopic substitution is invaluable.

- Examples of asymmetric tops: anthracene ($C_{14}H_{10}$), water (H_2O), nitrogen dioxide (NO_2)

3.4 Structure of rotational spectrum

- **Linear molecules**

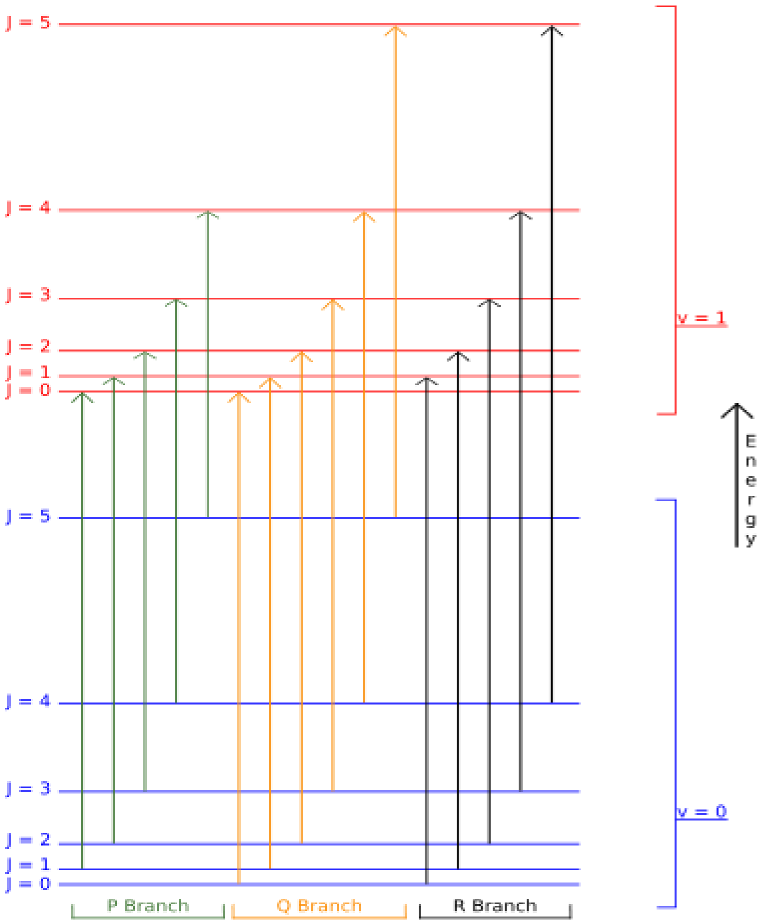


Figure 4.1.1: An energy level diagram showing some of the transitions involved in the IR vibration-rotation spectrum of a linear molecule: P branch (where $\Delta J = -1$), Q branch (not always allowed, $\Delta J = 0$) and R branch ($\Delta J = 1$)

Source: http://en.wikipedia.org/wiki/Rotational_spectroscopy"

These molecules have two degenerate modes of rotation ($I_B = I_C$, $I_A = 0$). Since we cannot distinguish between the two modes, we need only one rotational quantum number (J) to describe the rotational motion of the molecule.

The rotational energy levels ($F(J)$) of the molecule based on rigid rotor model can be expressed as,

$$F\left(J\right) = \tilde{B}_e J\left(J+1\right) \qquad J = 0, 1, 2, ...$$

where $\tilde{B}_e$ is the rotational constant of the molecule and is related to the moment of inertia of the molecule $I_B = I_C$ by,

$$\tilde{B}_e = \frac{h}{8\pi^2 c I_B}$$

Selection rules dictate that during emission or absorption the rotational quantum number has to change by unity i.e. $\Delta J = J' - J'' = \pm 1$. Thus the locations of the lines in a rotational spectrum will be given by,

$$\tilde{\nu}_{J' \leftrightarrow J''} = F\left(J'\right) - F\left(J''\right) = 2\tilde{B}_e\left(J''+1\right) \qquad J'' = 0, 1, 2, ...$$

where J'' denotes the lower energy level and J' denotes higher energy level involved in the transition. The height of the lines is determined by the distribution of the molecules in the different levels and the probability of transition between two energy levels.

We observe that, for a rigid rotor, the transition lines are equally spaced in the wavenumber space. However, this is not always the case, except for the rigid rotor model. For non-rigid rotor model, we need to consider changes in the moment of inertia of the molecule. Two primary reasons for this are,

- **Centrifugal distortion:**

When a molecule rotates, the centrifugal force pulls the atoms apart. As a result, the moment of inertia of the molecule increases, thus decreasing $\tilde{B}_e$. To account for this a centrifugal distortion correction term is added to the rotational energy levels of the molecule.

$$F(J) = \tilde{B}_e J(J+1) - \tilde{D}_e J^2 (J+1)^2 \qquad J = 0, 1, 2, \ldots$$

where $\tilde{D}_e$is the centrifugal distortion constant.

Accordingly the line spacing for the rotational mode changes to,

$$\tilde{\nu}_{J' \leftrightarrow J''} = 2\tilde{B}_e (J''+1) - 4\tilde{D}_e (J''+1)^3 \qquad J'' = 0, 1, 2, \ldots$$

- **Effect of vibration on rotation:**

A molecule is always in vibration. As the molecule vibrates, its moment of inertia changes. Further there is a fictitious force, Coriolis coupling, between the vibrational motions of the nuclei in the rotating (non-inertial) frame. However, as long as the vibrational quantum number does not change (i.e. the molecule is in only one state of vibration), the effect of vibration on rotation is not important, because the time for vibration is much shorter than the time required for rotation. The Coriolis coupling is often negligible, too, if one is interested in low vibrational and rotational quantum numbers only.

- **Symmetric top**

The rotational motion of a symmetric top molecule can be described by two independent rotational quantum numbers (since two axes have equal moments of inertia, the rotational motion about these axes requires only one rotational quantum number for complete description). Instead of defining the two rotational quantum numbers for two independent axes, we associate one of the quantum number (*J*) with the total angular momentum of the molecule and the other quantum number (*K*) with the angular momentum of the axis which has different moment of inertia (i.e. axis *C* for oblate symmetric top and axis *A* for prolate symmetric tops). The rotational energy *F*(*J*,*K*) of such a molecule, based on rigid rotor assumptions can be expressed in terms of the two previously defined rotational quantum numbers as follows,

$$F\left(J,K\right)=\tilde{B}J\left(J+1\right)+\left(\tilde{A}-\tilde{B}\right)K^2 \qquad J=0,1,2,... \quad \text{and} \quad K=-J,-J+1,...,-1,0,1,...,J-1,J$$

where $\tilde{B}=\frac{h}{8\pi^2cI_B}$ and $\tilde{A}=\frac{h}{8\pi^2cI_A}$ for a *prolate* symmetric top molecule or $\tilde{A}=\frac{h}{8\pi^2cI_C}$ for an *oblate* molecule.

Selection rule for these molecules provide the guidelines for possible transitions. Accordingly,

$$\Delta J=\pm 1 \quad \text{and} \quad \Delta K=0.$$

This is so because *K* is associated with the axis about which the molecule is symmetric and hence has no net dipole moment in that direction. Thus there is no interaction of this mode with the light particles (photon).

This gives the transition wavenumbers of,

$$\tilde{\nu}_{J'\leftrightarrow J'',K} = F\left(J',K\right) - F\left(J'',K\right) = 2\tilde{B}\left(J''+1\right) \qquad J'' = 0,1,2,\ldots$$

which is the same as in the case of a linear molecule.

In case of non-rigid rotors, the first order centrifugal distortion correction is given by,

$$F\left(J,K\right) = \tilde{B}J\left(J+1\right) + \left(\tilde{A}-\tilde{B}\right)K^2 - \tilde{D}_J J^2\left(J+1\right)^2 - \tilde{D}_{JK}J\left(J+1\right)K^2 - D_K K^4 \qquad J$$

J = 0,1,2, ……

The suffixes on the centrifugal distortion constant *D* indicate the rotational mode involved and are not a function of the rotational quantum number. The location of the transition lines on a spectrum is given by,

$$\tilde{\nu}_{J'\leftrightarrow J'',K} = F\left(J',K\right) - F\left(J'',K\right) = 2\tilde{B}\left(J''+1\right) - 4D_J\left(J''+1\right)^3 - 2D_{JK}\left(J''+1\right)K^2 \qquad J'' = 0,1,2,\ldots$$

- **Spherical tops**

Unlike other molecules, spherical top molecules have no net dipole moment, and hence they do not exhibit a pure rotational spectrum.

- **Asymmetric tops**

The spectrum for these molecules usually involves many lines due to three different rotational modes and their combinations. The following analysis is valid for the general case and collapses to the various special cases described above in the appropriate limit.

From the moments of inertia one can define an asymmetry parameter κ as

$$\kappa = \frac{2B - A - C}{A - C}$$

which varies from -1 for a prolate symmetric top to 1 for an oblate symmetric top.

One can define a scaled rotational Hamiltonian dependent on J and κ. The (symmetric) matrix representation of this Hamiltonian is banded, zero everywhere but the main diagonal and the second subdiagonal. The Hamiltonian can be formulated in six different settings, dependent on the mapping of the principal axes to lab axes and handedness. For the most asymmetric, right-handed representation the diagonal elements are, for $|k| \leq J$

$$H_{k,k}(\kappa) = \kappa k^2$$

and the second off-diagonal elements (independent of κ) are

$$H_{k,k+2}(\kappa) = \sqrt{[J(J+1) - (k+1)(k+2)][J(J+1) - k(k+1)]}/2.$$

Diagonalising H yields a set of $2J + 1$ scaled rotational energy levels $E_k(\kappa)$. The rotational energy levels of the asymmetric rotor for total angular momentum J are then given by

$$\frac{A+C}{2} J(J+1) + \frac{A-C}{2} E_k(\kappa)$$

3.5 **Hyperfine interactions**:

In addition to the main structure that is observed in microwave spectra due to the rotational motion of the molecules, a whole host of further interactions are responsible for small details in the spectra, and the study of these details provides a very deep understanding of molecular quantum mechanics. The main interactions responsible for small changes in the spectra (additional splittings and shifts of lines) are due to magnetic and electrostatic interactions in the molecule (Wikipedia, 2009). The particular strength of such interactions differs in different molecules, but in general, the order of these effects (in decreasing significance) is:

1. *electron spin* - *electron spin interaction* (this occurs in molecules with two or more unpaired electrons, and is a magnetic-dipole / magnetic-dipole interaction)
2. *electron spin* - *molecular rotation* (the rotation of a molecule corresponds to a magnetic dipole, which interacts with the magnetic dipole moment of the electron)
3. *electron spin* - *nuclear spin interaction* (the interaction between the magnetic dipole moment of the electron and the magnetic dipole moment of the nuclei (if present)).
4. *electric field gradient* - *nuclear electric quadrupole interaction* (the interaction between the electric field gradient of the electron cloud of the molecule and the electric quadrupole moments of nuclei (if present)).
5. *nuclear spin* - *nuclear spin interaction* (nuclear magnetic moments interacting with one another).

These interactions give rise to the characteristic energy levels that are probed in "magnetic resonance" spectroscopy such as NMR and ESR, where they represent the "zero field splittings" which are always present.

Activity A

(a) Define the term spectroscopy.

(b) Explain the theory of rotational spectroscopy.

3.6 Experimental determination of the spectrum

Fourier transform infrared (FTIR) spectroscopy can be used to experimentally study rotational spectra. Typically spectra at these wavelengths involve rovibrational excitation, i.e., excitation of both a vibrational and a rotational mode of a molecule.

Traditionally, microwave spectra were determined using a simple arrangement in which low pressure gas was introduced to a section of waveguide between a microwave source (of variable frequency) and a microwave detector. The spectrum was obtained by sweeping the frequency of the source while detecting the intensity of the transmitted radiation. This experimental arrangement has a major difficulty related to the propagation of microwave radiation through waveguides. The physical size of the waveguide restricts the frequency of the radiation that can be transmitted through it. For a given waveguide size (such as X-band) there is a cutoff frequency, and microwave radiation with smaller frequencies (longer wavelengths) cannot be propagated through the waveguide. Additionally, as the frequency is increased, additional modes of propagation become possible, which correspond to different velocities of the radiation propagating down the waveguide (this can be envisaged as the radiation bouncing down the guide, at different angles of reflection). The net result of these considerations is that each size of waveguide is only useful over a rather narrow range of frequencies and must be physically swapped out for a different size of waveguide once this frequency range is exceeded (Wikipedia, 2009).

Within the last two years, a further development of Fourier Transform Microwave Spectroscopy has occurred, which may well introduce a new renaissance into microwave spectroscopy. This is the use of "Chirped Pulses" to provide an electromagnetic wave that has as its Fourier Transform a very wide range of microwave frequencies. (see University of Virginia, Chemistry Department website).

3.7 Applications

Microwave spectroscopy is commonly used in physical chemistry to determine the structure of small molecules (such as ozone, methanol, or water) with high precision. Other common techniques for determining molecular structure, such as X-ray crystallography don't work very well for some of these molecules (especially the gases) and are not as precise. However, microwave spectroscopy is not useful for determining the structures of large molecules such as proteins.

Microwave spectroscopy is one of the principal means by which the constituents of the universe are determined from the earth. It is particularly useful for detecting molecules in the interstellar medium (ISM). One of the early surprises in interstellar chemistry was the existence in the ISM of long chain carbon molecules. It was in attempting to research such molecules in the laboratory that Harry Kroto was led to the laboratory of Rick Smalley and Robert Curl, where it was possible to vaporize carbon under enormous energy conditions. This collaborative experiment led to the discovery of C_{60}, buckminsterfullerene, which led to the award of the 1996 Nobel prize in chemistry to Kroto, Smalley and Curl.

Activity B

Explain what you understand by each of the following: (a) Centrifugal distortion (b) Hyperfine interactions

4.0 Conclusion

Rotational spectroscopy or microwave spectroscopy studies the absorption and emission of electromagnetic radiation (typically in the microwave region of the electromagnetic spectrum) by molecules associated with a corresponding change in the rotational quantum number of the molecule.

5.0 Summary

In this unit we have learnt that;

(i) interpretation of spectra provides fundamental information on atomic and molecular energy levels, the distribution of species within those levels, the nature of processes involving change from one level to another, molecular geometries, chemical bonding, and interaction of molecules in solution;

(ii) in quantum mechanics the free rotation of a molecule is quantized, that is the rotational energy and the angular momentum can only take certain fixed values; what these values are is simply related to the moment of inertia, *I*, of the molecule and

(iii) Aaconvenient way to look at the molecules is to divide them into four different classes (based on the symmetry of their structure).

6.0 Tutor marked assignment

(a) Explain the theory of rotational spectroscopy.

(b) Draw energy diagram for rotational spectroscopy.

(c) Explain how rotational spectroscopy could be used to determine the structures of small molecules.

(d) Classify molecules based on rotational behaviour.

7.0 Further reading and references

Atkins, P. W. (1982). Physical Chemistry, (2_{nd} ed.), Oxford, Oxford University Press.

Barrow, G. M. (1982). Physical Chemistry (4_{th} ed.), Auckland, McGraw-Hill.

Brown and Carrington, *Rotational Spectroscopy of Diatomic molecules*, Retrieved August 2, 2009 from website: "http://en.wikipedia.org/wiki/Rotational_spectroscopy"

Harry Kroto, Dover. *Molecular Rotation Spectra*, Retrieved August 2, 2009 from website: "http://en.wikipedia.org/wiki/Rotational_spectroscopy"

Mcquarrie, D. A. *Quantum Mechanics*. Retrieved August 2, 2009 from website: "http://en.wikipedia.org/wiki/Rotational_spectroscopy"

Townes and Schawlow, Dover.*Microwave Spectroscopy*, Retrieved August 2, 2009 from website: "http://en.wikipedia.org/wiki/Rotational_spectroscopy"

Wikipedia, (2009). Retrieved August 2, 2009 from website: "http://en.wikipedia.org/wiki/Rotational_spectroscopy"

Module 4: Theory of Molecular Spectroscopy

Unit 2: Vibrational Spectroscopy

Contents

1.0 Introduction 262

2.0 Objectives........ 262

3.0 Definition of vibration spectroscopy 263

  3.1 Vibrational coordinates........ 264

    3.1.1 Internal coordinates........ 264

    3.1.2 Symmetry-adapted coordinates 265

    3.1.3 Normal coordinates 266

  3.2 Newtonian mechanics........ 267

3.3 Quantum mechanics 268
3.4 Intensities 269
4.0 Conclusion 270
5.0 Summary 270
6.0 Tutor marked assignment 270
7.0 Further reading and references........ 271

1.0 Introduction

Spectroscopy was originally the study of the interaction between radiation and matter as a function of wavelength (λ). In fact, historically, spectroscopy referred to the use of visible light dispersed according to its wavelength, e.g. by a prism. Later the concept was expanded greatly to comprise any measurement of a quantity as function of either wavelength or frequency. Thus it also can refer to a response to an alternating field or varying frequency (ν). A further extension of the scope of the definition added energy (E) as a variable, once the very close relationship $E = h\nu$ for photons was realized (h is the Planck constant). A plot of the response as a function of wavelength—or more commonly frequency—is referred to as a spectrum (Wikipedia, 2009).

2.0 Objectives

By the end of this unit, you should be able to:

(a) define what vibrational spectroscopy is;
(b) explain the theory of vibration spectroscopy;
(c) explain vibrational coordinates and
(d) calculate the correct vibration frequencies using Newtonian mechanics

3.0 Definition of vibration spectroscopy

A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is known as a vibration frequency. A nonlinear molecule with n atoms has $3n-6$ normal modes of vibration, whereas a *linear* molecule has $3n-5$ normal modes of vibration as rotation about its molecular axis cannot be observed. A diatomic molecule thus has one normal mode of vibration. The normal modes of vibration of polyatomic molecules are independent of each other, each involving simultaneous vibrations of different parts of the molecule.

A molecular vibration is excited when the molecule absorbs a quantum of energy, E, corresponding to the vibration's frequency, ν, according to the relation $E=h\nu$, where h is Planck's constant. A fundamental vibration is excited when one such quantum of energy is absorbed by the molecule in its ground state. When two quanta are absorbed the first overtone is excited, and so on to higher overtones.

To a first approximation, the motion in a normal vibration can be described as a kind of simple harmonic motion. In this approximation, the vibrational energy is a quadratic function (parabola) with respect to the atomic displacements and the first overtone has twice the frequency of the fundamental. In reality, vibrations are anharmonic and the first overtone has a frequency that is slightly lower than twice that of the fundamental. Excitation of the higher overtones involves progressively less and less additional energy and eventually leads to dissociation of the molecule, as the potential energy of the molecule is more like a Morse potential.

The vibrational states of a molecule can be probed in a variety of ways. The most direct way is through infrared spectroscopy, as vibrational transitions typically require an amount of energy that corresponds to the infrared region of the spectrum. Raman spectroscopy, which typically uses visible light, can also be used to measure vibration frequencies directly.

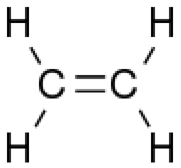
Vibrational excitation can occur in conjunction with electronic excitation (vibronic transition), giving vibrational fine structure to electronic transitions, particularly with molecules in the gas state. Simultaneous excitation of a vibration and rotations gives rise to vibration-rotation spectra.

3.1 Vibrational coordinates

The coordinate of a normal vibration is a combination of changes in the positions of atoms in the molecule. When the vibration is excited the coordinate changes sinusoidally with a frequency ν, the frequency of the vibration.

3.1.1 Internal coordinates

Internal coordinates are of the following types, illustrated with reference to the planar molecule ethylene,



- Stretching: a change in the length of a bond, such as C-H or C-C
- Bending: a change in the angle between two bonds, such as the HCH angle in a methylene group
- Rocking: a change in angle between a group of atoms, such as a methylene group and the rest of the molecule.
- Wagging: a change in angle between the plane of a group of atoms, such as a methylene group and a plane through the rest of the molecule,

- Twisting: a change in the angle between the planes of two groups of atoms, such as a change in the angle between the two methylene groups.
- Out-of-plane: Not present in ethene, but an example is in BF_3 when the boron atom moves in and out of the plane of the three fluorine atoms.

In a rocking, wagging or twisting coordinate the angles and bond lengths within the groups involved do not change. Rocking is distinguished from wagging by the fact that the atoms in the group stay in the same plane.

In ethene there are 12 internal coordinates: 4 C-H stretching, 1 C-C stretching, 2 H-C-H bending, 2 CH_2 rocking, 2 CH_2 wagging, 1 twisting. Note that the H-C-C angles cannot be used as internal coordinates as the angles at each carbon atom cannot all increase at the same time (Wikipedia, 2009).

3.1.2 Symmetry-adapted coordinates

Symmetry-adapted coordinates may be created by applying a projection operator to a set of internal coordinates. The projection operator is constructed with the aid of the character table of the molecular point group. For example, the four (un-normalised) C-H stretching coordinates of the molecule ethene are given by

$$Q_{s1} = q_1 + q_2 + q_3 + q_4$$

$$Q_{s2} = q_1 + q_2 - q_3 - q_4$$

$$Q_{s3} = q_1 - q_2 + q_3 - q_4$$

$Q_{s4} = q_1 - q_2 - q_3 + q_4$

where q_1 - q_4 are the internal coordinates for stretching of each of the four C-H bonds.

Illustrations of symmetry-adapted coordinates for most small molecules can be found in Nakamoto.

3.1.3 Normal coordinates

A normal coordinate, Q, may sometimes be constructed directly as a symmetry-adapted coordinate. This is possible when the normal coordinate belongs uniquely to a particular irreducible representation of the molecular point group. For example, the symmetry-adapted coordinates for bond-stretching of the linear carbon dioxide molecule, O=C=O are both normal coordinates:

- symmetric stretching: the sum of the two C-O stretching coordinates; the two C-O bond lengths change by the same amount and the carbon atom is stationary. $Q = q_1 + q_2$
- asymmetric stretching: the difference of the two C-O stretching coordinates; one C-O bond length increases while the other decreases. $Q = q_1 - q_2$

When two or more normal coordinates belong to the same irreducible representation of the molecular point group (colloquially, have the same symmetry) there is "mixing" and the coefficients of the combination cannot be determined *a priori*. For example, in the linear molecule hydrogen cyanide, HCN, The two stretching vibrations are

1. principally C-H stretching with a little C-N stretching; $Q_1 = q_1 + a\, q_2$ ($a << 1$)
2. principally C-N stretching with a little C-H stretching; $Q_2 = b\, q_1 + q_2$ ($b << 1$)

The coefficients a and b are found by performing a full normal coordinate analysis by means of the Wilson GF method.

3.2 Newtonian mechanics

Perhaps surprisingly, molecular vibrations can be treated using Newtonian mechanics, to calculate the correct vibration frequencies. The basic assumption is that each vibration can be treated as though it corresponds to a spring. In the harmonic approximation the spring obeys Hooke's law: the force required to extend the spring is proportional to the extension. The proportionality constant is known as a *force constant*, k. The anharmonic oscillator is considered elsewhere.

$$\mathrm{Force} = -kQ$$

By Newton’s second law of motion this force is also equal to a "mass", m, times acceleration.

$$\mathrm{Force} = m\frac{d^2Q}{dt^2}$$

Since this is one and the same force the ordinary differential equation follows.

$$m\frac{d^2Q}{dt^2} + kQ = 0$$

The solution to this equation of simple harmonic motion is

$$Q(t) = A\cos(2\pi\nu t); \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

A is the maximum amplitude of the vibration coordinate Q. It remains to define the "mass", m. In a homonuclear diatomic molecule such as N_2, it is half the mass of one molecule. In a heteronuclear diatomic molecule, AB, it is the reduced mass, μ given by

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

The use of the reduced mass ensures that the centre of mass of the molecule is not affected by the vibration. In the harmonic approximation the potential energy of the molecule is a quadratic function of the normal coordinate. It follows that the force-constant is equal to the second derivative of the potential energy.

$$f = \frac{\partial^2 V}{\partial Q^2}$$

When two or more normal vibrations have the same symmetry a full normal coordinate analysis must be performed. The vibration frequencies,ν_i are obtained from the , λ_i, of the matrix product ***GF***. ***G*** is a matrix of numbers derived from the masses of the atoms and the geometry of the molecule. ***F*** is a matrix derived from force-constant values. Details concerning the determination of the eigenvalues can be found in.

Activity A

Briefly explain the following terms: (a) spectroscopy (b) molecular vibration

3.3 Quantum mechanics

In the harmonic approximation the potential energy is a quadratic function of the normal coordinates. Solving the Schrödinger wave equation, the energy states for each normal coordinate are given by

$$E_n = \left(n + \frac{1}{2}\right) h \frac{1}{2\pi} \sqrt{\frac{k}{m}},$$

where *n* is a quantum number that can take values of 0, 1, 2 ... The difference in energy when *n* changes by 1 are therefore equal to the energy derived using classical mechanics.. Knowing the wave functions, certain selection rules can be formulated. For example, for a harmonic oscillator transitions are allowed only when the quantum number *n* changes by one,

$$\Delta n = \pm 1$$

but this does not apply to an anharmonic oscillator; the observation of overtones is only possible because vibrations are anharmonic. Another consequence of anharmonicity is that transitions such as between states n=2 and n=1 have slightly less energy than transitions between the ground state and first excited state. Such a transition gives rise to a hot band (Wikipedia, 2009).

3.4 Intensities

In an infrared spectrum the intensity of an absorption band is proportional to the derivative of the molecular dipole moment with respect to the normal coordinate. The intensity of Raman bands depends on .

Activity B

(a) Explain the theory of vibration spectroscopy.

(b) Explain what you understand by vibrational coordinates.

4.0 Conclusion

The vibrational states of a molecule can be probed in a variety of ways. The most direct way is through infrared spectroscopy, as vibrational transitions typically require an amount of energy that corresponds to the infrared region of the spectrum.

5.0 Summary

In this unit we have learnt that:

(a) a molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion
(b) the frequency of the periodic motion is known as a vibration frequency.
(c) a molecular vibration is excited when the molecule absorbs a quantum of energy, E, corresponding to the vibration's frequency.
(d) simultaneous excitation of a vibration and rotations gives rise to vibration-rotation spectra and
(e) the coordinate of a normal vibration is a combination of changes in the positions of atoms in the molecule.

6.0 Tutor marked assignment

1. Briefly discuss the vibrational coordinates of normal vibration giving relevant examples.
2. Give the usefulness of Newtonian mechanics and Quantum mechanics in vibrational spectroscopy.

7.0 Further reading and references

Atkins, P. W. (1982). Physical Chemistry, (2$_{nd}$ ed.), Oxford, Oxford University Press.

Barrow, G. M. (1982). Physical Chemistry (4$_{th}$ ed.), Auckland, McGraw-Hill.

Califano, S. (1976). *Vibrational states*, Wiley. Retrieved August 2, 2009 from Wikipedia encyclopedia website: "http://en.wikipedia.org/wiki/Molecular_vibration"

Cotton, F.A.(1962, 1971). *Chemical applications of group theory*, Wiley. Retrieved August 2, 2009 from Wikipedia encyclopedia website: "http://en.wikipedia.org/wiki/Molecular_vibration"

Gans, P. (1971). *Vibrating molecules*, Chapman and Hall. Retrieved August 2, 2009 from Wikipedia encyclopedia website: "http://en.wikipedia.org/wiki/Molecular_vibration"

Nakamoto K. (1997) *Infrared and Raman spectra of inorganic and coordination compounds*, (5th. Ed.), Part A, Wiley. Retrieved August 2, 2009 from Wikipedia encyclopedia website: "http://en.wikipedia.org/wiki/Molecular_vibration"

Sherwood, P.M.A. (1972) *Vibrational spectroscopy of solids*, Cambridge University Press. Retrieved August 2, 2009 from Wikipedia encyclopedia website: "http://en.wikipedia.org/wiki/Molecular_vibration"

Steele, D. (1971).*Theory of vibrational spectroscopy*, W.B. Saunders. Press. Retrieved August 2, 2009 from Wikipedia encyclopedia website: http://en.wikipedia.org/wiki/Molecular_vibration"

Wikipedia, (2009). Retrieved August 2, 2009 from website: http://en.wikipedia.org/wiki/Rotational_spectroscopy"

Wilson, E.B., Decius J.C. and Cross, P.C. (1955) *Molecular vibrations*, McGraw-Hill, (Reprinted by Dover, 1980). Press. Retrieved August 2, 2009 from Wikipedia encyclopedia website: "http://en.wikipedia.org/wiki/Molecular_vibration"

Module 4: Theory of Molecular spectroscopy

Unit 3: Vibrational-Rotational spectrocopy

Contents

1.0 Introduction 273

2.0 **Objectives**.. 2

3.0 Definition of vibrational and rotational transitions of diatomic molecules.................................... 274

  3.1 Selection rules 277

  3.2 Isotope effect 279

  3.4 The Vibrational wavefunctions and their properties 283

3.5 Symmetry relations. 284
3.6 Selection rules. 286
3.7 Force constants of acetylene. 288
3.8 Rotational levels and transitions. 289
3.9 Intensities and statistical weights. 291
4.0 Conclusion 293
5.0 Summary 293
6.0 Tutor marked assignment 294
7.0 Further reading and references. 294

1.0 Introduction

From the interpretations given to thermodynamic properties of gases, gas molecules are simultaneously rotating and vibrating. It follows that an absorption spectrum or a Raman spectrum of a gas might show the effects of changes in both rotational and vibrational energies.

2.0 Objectives

By the end of this unit, you should be able to:

(a) explain the vibrational and rotational transitions of diatomic molecules;
(b) relate the intensity of a spectral line to the population of the initial state;
(c) explain isotope effect and
(d) explain the vibrational and rotational transitions of polyatomic molecules;

3.0 Definition of vibrational and rotational transitions of diatomic molecules

High-resolution gas-phase IR spectra show information about the vibrational and rotational behavior of heteronuclear diatomic molecules (NIST, 2009). Vibrational transitions of HCl and DCl may be modeled by the harmonic oscillator when the bond length is near R_e. In this region, the potential energy can be calculated as:

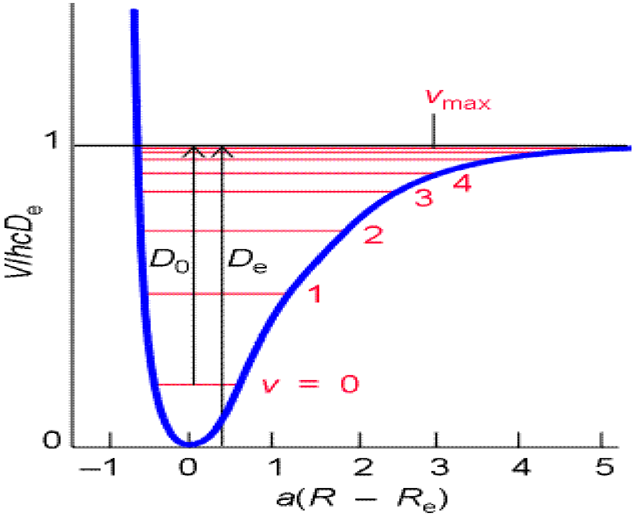


Figure 4.3.1; High-resolution gas-phase IR spectra

showing information about the vibrational and rotational behavior of heteronuclear diatomic molecules. Source: www.webbook.nist.gov/chemistry

$$E = \frac{1}{2}k(R - R_e)^2 \qquad (4.3.1)$$

where k is the force constant of the bond. The Schrödinger equation for a particle undergoing harmonic motion can be modified to give an equation to calculate the *allowed* vibrational energy levels:

$$E(\upsilon) = (\upsilon + 1/2)h\nu \qquad (4.3.2)$$

where h is Planck's constant, ν is the vibrational frequency, and the vibrational quantum number $\upsilon = 0, 1, 2, ...$

Of course, diatomic molecules do not remain stationary as they undergo vibration; they also rotate through space. The rigid rotor model may be used to approximate the rotational contribution to the IR spectrum of a diatomic molecule (NIST, 2009). For a rigid rotor, the allowed energy levels may be calculated as:

$$E(J) = \frac{h^2}{8\pi^2 I}J(J+1) \qquad (4.3.3)$$

where

$$I = \mu r^2, \quad \mu = \frac{m_1 m_2}{(m_1 + m_2)} \tag{4.3.4}$$

where J is the rotational quantum number (with integer values 0, 1, 2, ...), h is Planck's constant, and I is the **moment of inertia** for the molecule (calculated as shown using the **reduced mass**, μ, and with $r = r_e$). Note that the equation for $E(J)$ is not necessarily in cm^{-1}; you may have to use a conversion factor to get the desired units.

Adding these vibrational and rotational energy terms gives a first approximation of the value of its energy levels. However, we should also include terms which account for **anharmonicity**, **centrifugal distortion (stretching)**, and the interaction between vibration and rotation. An expression for the energy levels for the heteronuclear diatomic molecule in terms of wavenumbers (cm^{-1}) is:

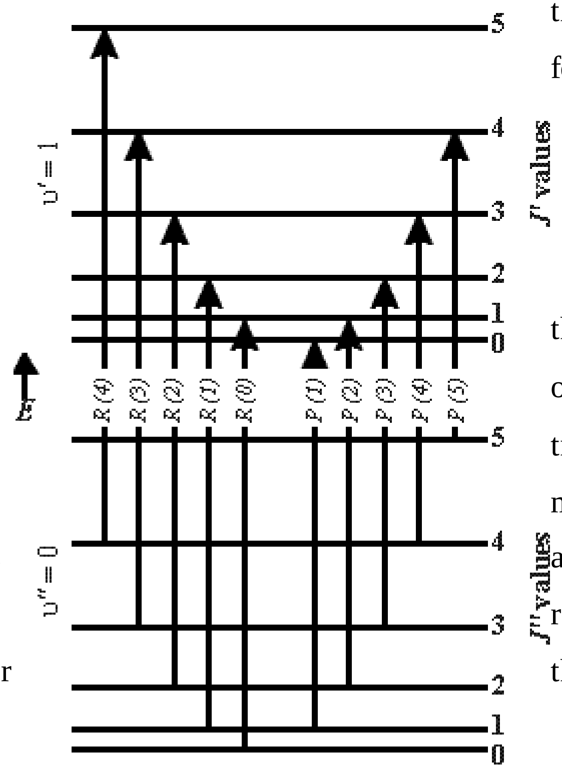
$$G(v, J) = \nu_e(v + 1/2) - \nu_e x_e(v + 1/2)^2 + B_e J(J + 1) - D_e J^2(J + 1)^2 - \alpha_e(v + 1/2)J(J + 1) \tag{4.3.5}$$

where ν_e is the frequency (which we, from now, will express in cm^{-1}, tilda is usually used on the top of ν, but we will omit it) for the molecule vibrating about the equilibrium bond distance r_e, and

$$B_e = \frac{h}{8\pi^2 I_e c} \tag{4.3.6}$$

The difference in energy, and thus the separation between adjacent lines (of the same isotope) in each branch of the IR spectrum, is related to B_e. The first and third terms of the equation for G account for the harmonic oscillator and rigid rotor behavior of the diatomic molecule; the second term accounts for anharmonicity (note it contains a constant, x_e); the fourth term takes into account centrifugal stretching, and the last term accounts for the interaction between vibration and rotation. The centrifugal stretching term may be neglected in this experiment since D_e is small, making this term significant only at high J values.

The last term accounts for the interaction between the vibration and rotation of the molecule; as the molecule vibrates, the moment of inertia changes and the rotation of the molecule is affected. The α_e term is large enough that the final term in the equation for G cannot be neglected.



3.1 Selection rules

For an harmonic oscillator, the selection rules require that $\Delta v = \pm 1$ and $\Delta J = \pm 1$. That is, when the vibrational transition (represented as $v + 1$ <-- v) occurs, J changes by +1 for the R branch and -1 for the P branch. Note that $\Delta J = 0$ is a forbidden transition for the diatomic species we are examining (as having no net spin or orbital angular momentum), so you will not see the Q branch corresponding to such a change. Also, since molecules are not exact harmonic oscillators, *i.e.* they possess some anharmonic character, weak overtones resulting from $\Delta v = \pm 2, \pm 3, \pm 4,...$ transitions are present, but we will not be concerned with these for the moment. These overtones are important to the blue color of water.

We are most interested in the fundamental transitions from the J'' levels of the vibrational ground state ($\upsilon'' = 0$) to the first excited state J' levels corresponding to $\upsilon' = 1$(see figure). The frequency in wavenumbers, ν, may be calculated for the R and P branches using the following equations:

$$\nu_R = \nu_o + (2B_e - 3\alpha_e) + (2B_e - 4\alpha_e)J'' - \alpha_e J''^2 \quad \text{for } J'' = 0, 1, 2, 3...$$

$$\nu_P = \nu_o - (2B_e - 2\alpha_e)J'' - \alpha_e J''^2 \quad \text{for } J'' = 1, 2, 3... \qquad (4.3.7)$$

Tfoffforbidden transition, ν_o, appears at a wavenumber between the *R(0)* and *P(1)* transitions (see figure below; the numbers in parentheses are J'' values). It is not, however, exactly between the two transitions. Note that the separation between the lines in the P branch increases as the J values increase while the separation between R branch lines decreases. This effect results from the interaction between the vibration and rotation; if there was no interaction, α_e would be zero and the separation between lines would be $2B_e$. The energy of the forbidden transition, ν_o, must be calculated using its relation to B_e and α_e using the equation

$$\nu = \nu_o + (2B_e - 2\alpha_e)m - \alpha_e m^2 \qquad (4.3.8)$$

where m is an integer and is defined as $m = J'' + 1$ for the R branch and $m = -J''$ for the P branch. The separation between adjacent lines of the same isotope in the IR spectrum is therefore

The values of B_e and α_e can be calculated from a plot of $\Delta\nu(m)$ versus m. Once these two values are determined, ν_o can be calculated using any

$$\Delta\nu(m) = \nu(m + 1) - \nu(m) = (2B_e - 3\alpha_e) - 2\alpha_e m \qquad (4.3.9)$$

value of *m* and the Eq.(4.3.9).

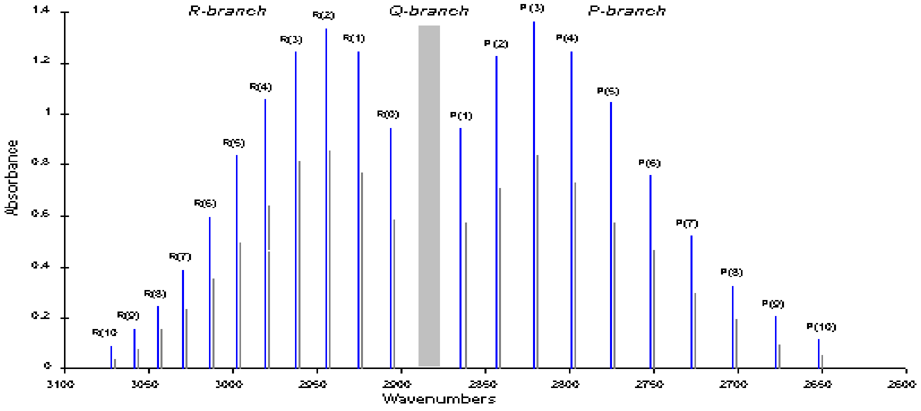


Figure 4.3.2: The fundamental absorption band under high resolution.
Source: www.webbook.nist.gov/chemistry

3.2 Isotope effect

We will discuss the isotope effect with reference to HCl; however, the other gases also exhibit isotope effects and you should analyze them as well. The most abundant form of HCl is $^{1}H^{35}Cl$. Another isotope of chlorine, ^{37}Cl, has a high natural abundance, however, and the lines for $^{1}H^{37}Cl$ are obvious in a high-resolution spectrum of HCl, right next to the $^{1}H^{35}Cl$ lines. In fact, the isotopic abundance of ^{35}Cl and ^{37}Cl may be calculated from the relative absorbance values in the IR spectrum (since absorbance is proportional to concentration). Though the change of an isotope (e.g., ^{35}Cl to ^{37}Cl) does not affect the equilibrium bond length r_e, or the force constant k for the molecule, varying an isotope does change μ, the reduced mass. Since the reduced mass affects the vibrational and rotational behavior or a molecule, the energy of its transitions are affected. For the harmonic oscillator, the vibrational transition occurs at the frequency $\nu_{harmonic}$, which is given by the equation

$$\nu_{harmonic} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (4.3.10)$$

The effect of the reduced mass on $\nu_{harmonic}$ (disregarding anharmonicity) can be presented in the form of the ratio

$$\frac{\nu^{*}_{harmonic}}{\nu_{harmonic}} = \sqrt{\frac{\mu}{\mu^{*}}} \qquad (4.3.11)$$

where the asterisk simply denotes a different isotope (for convenience, use the asterisk to denote the heavier isotope). For the effect of different isotopes on rotation, a similar relationship can be derived as

$$\frac{B^{*}_{e}}{B_{e}} = \frac{\mu}{\mu^{*}} \qquad (4.3.12)$$

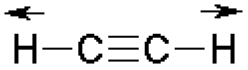
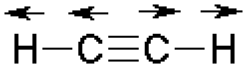
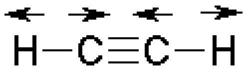
Of course, these effects apply to isotopes of hydrogen as well as chlorine.

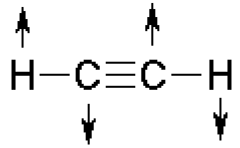
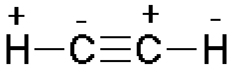
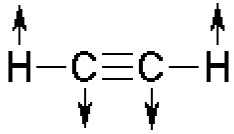
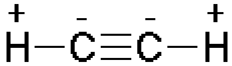
3.3 Vibrational and rotational transitions of polyatomic molecules; acetylene

Vibrational levels and wavefunctions. Acetylene is known to be a symmetric linear molecule with $D_{oo\,h}$ point group symmetry and $3N - 5 = 7$ vibrational *normal modes*, as depicted in Table 4.3.1. Symmetry is found to be an invaluable aid in understanding the motions in polyatomic molecules. Group theory shows that each vibrational coordinate and each vibrational energy level, along with its associated wavefunction, must have a symmetry corresponding to one of the symmetry species of the molecular point group. The D_{ooh} symmetry species corresponding to the different types of atomic motion in acetylene are indicated in the table. Motions that retain the center of inversion symmetry, such as the ν_1, ν_2, and ν_4, modes of Table 4.3.1, are labeled **g** (gerade, German for even) while those for which the displacement vectors are reversed on inversion are labeled **u** (ungerade, odd). Modes involving motion along the molecular axis (z) are called parallel vibrations and labeled Σ while those involving perpendicular motion are labeled Π and are doubly degenerate since equivalent bending can occur in either x or y directions. From the appearance of the nuclear displacements, it can be seen that only the ν_3 and ν_5 modes produce an oscillating change in the zero dipole moment of the molecule and hence give rise to infrared absorption.

Table 4.3.1: Fundamental vibrational modes of acetylene. Source: (NIST, 2009)

Source: www.webbook.nist.gov/chemistry

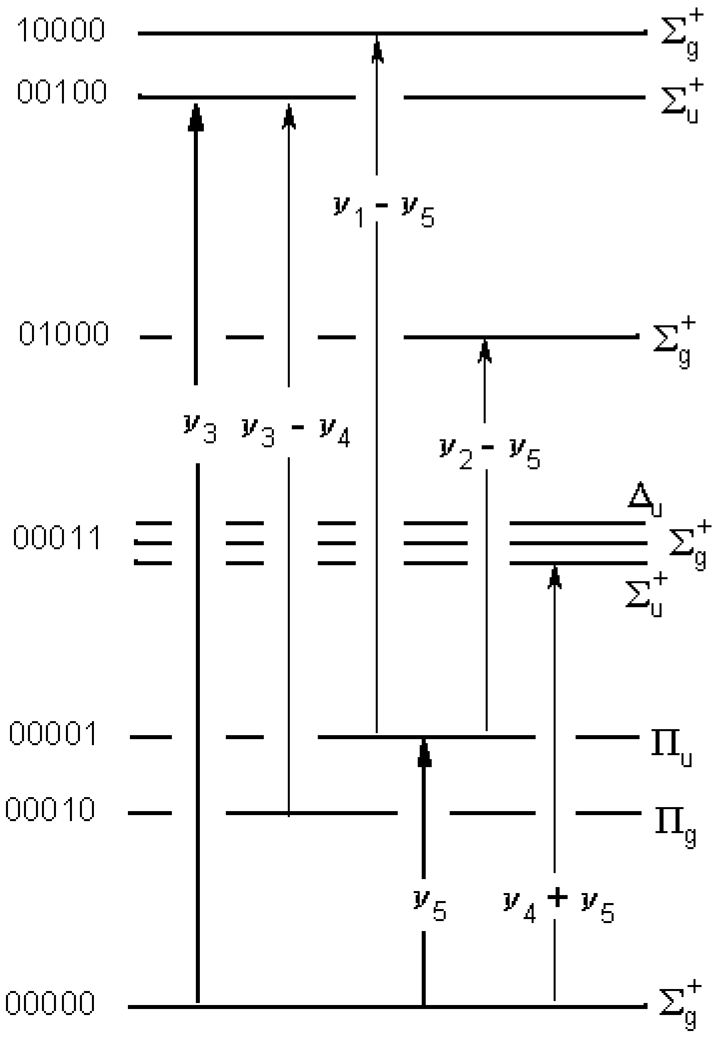
Normal Mode		Symmetry Species	Description	Activity Band Type	Frequency (cm^{-1})	
					C_2H_2	C_2D_2
	ν_1	Σ_g^+	Sym.CH stretch	R*p*, ‖	3372.8	2705.2
	ν_2	Σ_g^+	CC stretch	R*p*, ‖	1974.3	1764.8
	ν_3	Σ_u^+	Antisym.CH stretch	IR, ‖	3294.8	2439.2

	$\}\nu_4$	Π_g	Sym. Bend	R*dp*, ⊥	612.9	511.5
						
	$\}\nu_5$	Π_u	Antisym. Bend	IR, ⊥	730.3	538.6
						

From the harmonic-oscillator model of quantum mechanics, the term value G for the vibrational energy levels for a linear polyatomic molecule can be written as

$$G(v_1, v_2, \ldots) = \sum_{i=1}^{3N-5} \nu_i \left(v_i + \tfrac{1}{2}\right) \qquad (4.3.15)$$

where ν_i is the vibrational frequency of mode *i* measured in cm^{-1}. Additional anharmonicity corrections, analogous to $\nu_e x_e$, for diatomic molecules, can be added; but these are hopefully small (1-5% of ν_i) and will be neglected in this discussion. The energy levels of some of the states of acetylene are shown in Figure to the right. Each level is characterized by a set of harmonic oscillator quantum numbers $v_1v_2v_3v_4v_5$, shown at the left of the figure. The *fundamental* transitions from the ground state are those in which only one of the five quantum numbers increases from 0 to 1; the two infrared active fundamentals ν_3 and ν_5 are indicated with bold arrows in the figure.



Activity A

Briefly explain the vibrational and rotational transitions of diatomic molecules.

3.4 The vibrational wavefunctions and their properties

The set of quantum numbers of a level also labels the corresponding wavefunction, which, approximately at low vibrational energy, can be approximated as a product of harmonic oscillator wavefunctions in the separable 'normal coordinates', *Q*:

$$\Psi = \psi_{v1}(Q_1)\,\psi_{v2}(Q_2)\,\psi_{v3}(Q_3)... \qquad (4.3.16)$$

where each of the one dimensional wavefunctions have the conventional SHO form

$$
\begin{aligned}
\psi_0 &= \left(\frac{\gamma_i}{\pi}\right) \exp[-\gamma_i Q_i^2 / 2] \\
\psi_1 &= \left(\frac{4\gamma_i}{\pi}\right) \exp[-\gamma_i Q_i^2 / 2]\gamma_i^{1/2} Q_i \\
\psi_2 &= \left(\frac{\gamma_i}{4\pi}\right) \exp[-\gamma_i Q_i^2 / 2](2\gamma_i Q_i^2 - 1)
\end{aligned}
\qquad (4.3.17)
$$

where $\gamma_i = k_i/h$ and k_i is the quadratic force constant and ν_i is the vibrational frequency in each of the normal coordinate directions. The function ψ is even or odd depending on the parity of the Hermite polynomial, which is of order υ in the displacement. In general, this displacement may be a combination of bond stretches and bends that all occur at the same frequency with a given phase relation to each other.

The precise combination that characterizes a 'normal coordinate' displacement is obtained by solution of Newton's equations.

3.5 Symmetry relations.

Each normal coordinate Q_i, and every wavefunction involving products of the normal coordinates, must transform under the symmetry operations of the molecule as one of the symmetry species of the molecular point group. The ground-state function in Eq. (17) is a Gaussian exponential function that is quadratic in Q, and examination shows that this is of Σ_g^+ symmetry for each normal coordinate, since it is unchanged by any of the $D_{oo\,h}$ symmetry operations. From group theory, the symmetry of a product of two functions is deduced from the symmetry species for each function by a systematic procedure discussed in detail in. The results for the $D_{oo\,h}$ point group applicable to acetylene can be summarized as follows:

$$
\begin{array}{ll}
g \times g = u \times u = g & g \times u = u \times g = u \\
\Sigma^{+} \times \Sigma^{+} = \Sigma^{-} \times \Sigma^{-} = \Sigma^{+} & \Sigma^{+} \times \Sigma^{-} = \Sigma^{-} \\
\Sigma^{+} \times \Pi = \Sigma^{-} \times \Pi = \Pi & \Sigma^{+} \times \Delta = \Sigma^{-} \times \Delta = \Delta \\
\Pi \times \Pi = u + \Sigma^{-} + \Delta & \Delta \times \Delta = \Sigma^{+} + \Sigma^{-} + \Gamma \\
\Pi \times \Delta = \Pi + \Phi &
\end{array}
\qquad (4.3.18)
$$

Application of these rules shows that the product of two or more Σ_g^+ functions has symmetry Σ_g^+, hence the product function for the ground state level (00000) is of Σ_g^+ symmetry.

From Eq. (17), it is apparent that the symmetry species of a level with $\nu_i = 1$ is the same as that of the coordinate Q_i. In the case of a degenerate level such as (00001), there are two wavefunctions involving the degenerate Q_{5x}, Q_{5y}, pair of symmetry Π_u,. The symmetry of combination levels involving two *different* degenerate modes is obtained according to the above rules and, for example, for the (00011) level, one obtains $\Sigma_g^+ \times \Sigma_g^+ \times \Sigma_g^+ \times \Pi_g \times \Pi_u = \Sigma_u^+ + \Sigma_u^- + \Delta_u$. Thus one sees that the product of two degenerate functions gives rise to multiplets of different symmetries. For *overtone* levels of *degenerate* modes, a more detailed analysis is necessary in which it is found that levels such as (00020), (00003), and (00004) consist of multiplets of symmetry and $(\Sigma^+ + \Delta)$, $(\Pi + \Phi)$, and $(\Sigma^+ + \Delta + \Gamma)$, respectively.

From such considerations, the symmetry species of each wavefunction associated with an energy level is determined, and these are indicated at the right in the previous Figure. It is important to realize that this symmetry label is the correct one for the true wavefunction, even though deduced from an approximate harmonic oscillator model. This is significant because transition selection rules based on symmetry are *exact* whereas, for example, the usual harmonic oscillator constraint that $\Delta\upsilon = \pm 1$ is only *approximate* for real molecules.

3.6 Selection rules.

The probability of a transition between two levels i and j in the presence of infrared (electric dipole) radiation is given by the transition moment P_{ij}

$$P_{ij} = \int \psi_i \, \mu \, \psi_j \, d\tau \qquad (4.3.19)$$

For a given molecule, P_{ij} is a physical quantity with a unique numerical value that must remain unchanged by any molecular symmetry operation such as rotation or inversion. Hence to have a nonzero value, P_{ij} must be totally symmetric, *i.e.* $\Gamma(\psi_i) \times \Gamma(\mu) \times \Gamma(\psi_j) = \Sigma_g^+$ where $\Gamma(\psi_i)$ denotes the symmetry of ψ_i **,** etc. The dipole moment component μ_z, and the equivalent pair μ_x and μ_y are of symmetries Σ_u^+ and Π_u, respectively, for the $D_{\infty h}$ point group and are usually indicated at the far right in point group (or character) tables. From this and the rules of Eq. (19) it follows that, for a transition between two levels to be infrared-allowed, it is necessary that the symmetry species of the product of the two wavefunctions be the same as one of the dipole components. Thus from the Σ_g^+ ground vibronic state of acetylene, transition to the Σ_u^- or Δ_u members the (00011) multiplet is forbidden while that to the Σ_u^+ level is allowed by the μ_z dipole component. Transitions involving μ_z, are termed *parallel* bands while those involving μ_x and μ_y called *perpendicular bands*, because of the angle the dipole moment makes with the symmetry axis of the molecule

In the case of a Raman transition, the same symmetry arguments apply, except that the dipole function u must be replaced by the polarizability tensor elements a_{zz}, a_{xx}, a_{xy}, etc. For molecules of $D_{oo\ h}$ symmetry, these elements belong to the symmetry species Σ_g^+, Π_g, and Δ_g so that the condition for a Raman-active transition is that the product $\Gamma(\psi_i) \times \Gamma(\psi_j)$ include one of these species. Thus from the Σ_g^+ ground state of acetylene, Raman transitions to the (10000) Σ_g^+, (01000) Σ_g^+, and (00010) Π_g levels are allowed and can be used to determine the ν_1 , ν_2, and ν_4 fundamental frequencies respectively. As can be seen in Table 1, these three modes do not produce a dipole change as vibration occurs and thus these transitions are absent from the infrared spectrum. This is an example of the "rule of mutual exclusion," which applies for IR/Raman transitions of molecules with a centre of symmetry.

Although direct access to the (10000), (01000), and (00010) levels from the (00000) ground state level by infrared absorption is thus rigorously forbidden by symmetry, access from molecules in the (00010) or (00001) levels can be symmetry-allowed. For example, $\Gamma(00001) \times \Gamma(10000) = \Pi_u \times \Sigma_g^+ = \Pi_u = \Gamma(\mu_{x,y})$ and so the transition between these levels, sometimes termed a *difference band*, $\nu_1 - \nu_5$, is not formally forbidden. As can be seen in Figure above, the frequency ($\nu_1 - \nu_5$) can be added to the fundamental frequency ν_5 to give the *exact* value of ν_1, the (10000) - (0000) spacing. Similarly the $\nu_2 - \nu_5$ and $\nu_3 - \nu_4$ difference bands are infrared-active and can be combined with ν_5 and ν_3, to deduce ν_2 and ν_4, respectively. Such difference bands are detectable for acetylene but will, of course, have low intensity because they originate in vibrationally excited levels that have a small Boltzmann population at room temperature. The intensity of such bands increases with temperature, hence they are also termed *"hot band*" transitions.

Other non-fundamental bands often appear in infrared spectra and can be used to get an estimate of the fundamental frequencies. For example, from the ground state of acetylene, an infrared transition to the (00011) level is permitted and is termed the $\nu_4 + \nu_5$ *combination* band. The difference $(\nu_4 + \nu_5) - \nu_5$ can be used as an estimate of ν_4, but it should be noted that this is actually the separation between levels (00011) and

(00001) and not the separation between (00010) and (00000), which is a better measure of the frequency of the ν_4 normal mode in the harmonic approximation. Because of anharmonicity effects, these two separations are *not identical* and hence the determination of fundamental frequencies from difference bands is to be preferred.

3.7 Force constants of acetylene.

From the vibrational frequencies of the normal modes one can calculate the force constants for the different bond stretches and angle bends in the C_2H_2 molecule. In the most complete valence-bond, harmonic-oscillator approximation, the potential energy for C_2H_2 can be written as

$$U = \tfrac{1}{2}\, k_r(r_1^2 + r_2^2) + \tfrac{1}{2}\, k_R R^2 + \tfrac{1}{2}\, k_\delta\, (\delta_1^2 + \delta_2^2) + k_{rr} r_1 r_2 + k_{rR} R(r_1 + r_2) + k_{\delta\delta}\delta_1\delta_2 \qquad (4.3.20)$$

where r and R refer, respectively, to the stretching of the CH and CC bonds and represents bending of the H-C-C angle from its equilibrium value. The interaction constants k_{rr}, k_{rR}, and $k_{\delta\delta}$ characterize the coupling between the different vibrational coordinates and are usually small compared to the principal force constants k_r, k_R and k_δ.

The normal modes are combinations of r, R, and δ coordinates that provide an accurate description of the atomic motions as vibration takes place. These combinations must be chosen to have a symmetry corresponding to the symmetry species of the vibration. Consequently, for example, there is no mixing between the orthogonal axial stretches and the perpendicular bending modes and U contains no cross terms such as $r\delta$ or $R\delta$. The process of finding the correct combination of coordinates, termed a normal coordinate analysis, basically involves the solution of

Newton's equations of motion in the form of a normal coordinate analysis. This solution also gives the vibrational frequencies in terms of the force constants, atomic masses, and geometry of the molecule.

Such an analysis yields the following results for this case (linear HCCH)

$$4\pi^2\nu_1^2 + 4\pi^2\nu_2^2 = (k_r + k_{rr})(1/m_H + 1/m_C) + 2(k_R - k_{rR})/m_C \qquad (4.3.21a)$$

$$4\pi^2\nu_1^2\ 4\pi^2\nu_2^2 = 2[(k_r + k_{rr})k_R - 2k_{rR}^2)/m_C m_H \qquad (4.3.21b)$$

$$4\pi^2\nu_3^2 = (k_r - k_{rr})(1/m_H + 1/m_C) \qquad (4.3.21c)$$

$$4\pi^2\nu_4^2 = (k_\delta - k_{\delta\delta})[(1/R_{CH}^2 m_H + (1/R_{CH} + 2/R_{CC})^2/m_C] \qquad (4.3.21d)$$

$$4\pi^2\nu_5^2 = (k_\delta + k_{\delta\delta})(1/m_H + 1/m_C)/R_{CH}^2 \qquad (4.3.21e)$$

When C_2D_2 frequencies are used, m_H should be replaced by m_D. The force constants for acetylene can be calculated from these relations using the measured vibrational frequencies and the bond lengths can be determined from the rotational analysis described below. If one expresses the frequencies in cm^{-1} units and the masses in atomic mass units, the factors $4\pi^2$ should be replaced by $4\pi^2c^2/N_0 = 5.892 \times 10^{-5}$. This substitution gives the force constants k_r, k_R, k_{rr}, and k_{rR} in N/m units and the bending constants k_δ and $k_{\delta\delta}$ in units of N m.

3.8 Rotational levels and transitions.

$$F_v(J) = B_v[J(J + 1) - l^2] - D_v[J(J + 1) - l^2]^2 \qquad (4.3.22)$$

The vibrational-rotational energy levels for a linear molecule are similar to those for a diatomic molecule and, to a good approximation, are given in cm^{-1} units by the sum $G(v_1,v_2,...) + F_v(J)$ where

The general label v characterizes the set $v_1v_2v_3...$ and is added to F_v to account for the fact that the rotational constant B and centrifugal distortion constant D change slightly with vibrational level. B_v is related to the moment of inertia I_v by the equation:

$$B_v = \frac{h}{8\pi^2 I_v c} \qquad (4.3.23)$$

where

$$I_v = \sum_{i=1}^{N} m_i r^2_i \qquad (4.3.24)$$

and the sum is over all atoms in the molecule, having mass m_i and located a distance r_i from the **center-of-mass** of the molecule. The quantum number l characterizes the vibrational angular momentum about the linear axis and is 0, 1, 2, . . . for levels of symmetries Σ, Π, Δ, ..., respectively. This angular momentum derives from a rotary motion produced about the linear axis by a combination of the degenerate x and y bending motions. For acetylene, there are two bending modes, requiring l_4 and l_5 quantum numbers, which are sometimes shown as superscripts to the ν_4 and ν_5 labels.

The allowed changes in the rotational quantum number J are $\Delta J = \pm 1$ for parallel (Σ_u^+) transitions and $\Delta J = 0, \pm 1$ for perpendicular (Π_u) transitions. Parallel transitions such as ν_3 for acetylene thus have P ($\Delta J = -1$) and R ($\Delta J = +1$) branches with a characteristic minimum or 'missing line', between them, as shown for diatomic molecules such as HCl. However, perpendicular transitions such as ν_5 for acetylene and ν_2 for HCN have a strong central Q branch ($\Delta J = 0$) along with P and R branches. This characteristic *PQR* versus *PR* band shape is quite obvious in the spectrum and is a useful aid in assigning the symmetries of the vibrational levels involved in the infrared transitions of a linear molecule.

The individual lines in a Q branch are resolved only under very high resolution, but the lines in the P and R branches are easily discerned at a resolution of 1 cm^{-1} or better. As discussed in relation to the IR spectrum of HCl, it is possible to represent both P and R transition frequencies with a single relation:

$$\nu_m = \nu_o + B''l''^2 - B'l'^2 + (B'' + B')m + (B' - B'')m^2 - 4D_e m^3 \tag{4.3.25}$$

Here ν_o is the rotationless transition frequency corresponding to ΔG, the spacing between the two vibrational levels with J = 0. B' and B'' are the rotational constants of the upper and lower states, respectively, and the index $m = -J$ for P branch lines, $m = J + 1$ for R branch lines. The centrifugal distortion constants are neglected in this analysis since they are extremely small (typically 10^{-6} cm^{-1}), *i.e.* $D_e'' = D_e' = D_e$.

3.9 Intensities and statistical weights.

The absolute absorption intensity of a vibrational-rotational transition is proportional to the square of the transition moment P_{ij} times the population in the lower state. P_{ij} varies only slightly for different rotational levels so that the principal factors determining the relative intensity are the degeneracy and the Boltzmann weight for the lower level

$$I_J \sim g_I g_J \exp\left[-hcBJ(J+1)/kT \right] \qquad (4.3.26)$$

The rotational degeneracy g_J is $2J + 1$, and the nuclear-spin degeneracy g_I, varies with rotational level only when the molecule contains symmetrically equivalent nuclei (NIST, 2009). Briefly, the total wavefunction, Ψ_{tot}, for molecules with equivalent nuclei must obey certain symmetry requirements upon exchange, as determined by the Pauli principle. Exchange of nuclei with half-integral spin (Fermions), such as protons (I = 1/2), must produce a sign change in Ψ_{tot}. Nuclei with integral nuclear spin, such as deuterium (I = 1), obey Bose-Einstein statistics and are called bosons; for these the sign of Ψ_{tot}, is unchanged by interchange of the equivalent particles. The total wavefunction can be written, approximately, as a product function

$$\Psi_{tot} = \psi_{elec}\psi_{vib}\psi_{rot}\,\psi_{nspin} \qquad (4.3.27)$$

For the ground vibrational state of acetylene, $\psi_{elec}\psi_{vib}$ is symmetric with respect to nuclear exchange so that $\psi_{rot}\psi_{nspin}$, must be antisymmetric for C_2H_2, symmetric for C_2D_2. For linear molecules the ψ_{rot} functions are spherical harmonics that are symmetric for even **J,** antisymmetric for odd J. The ψ_{nspin} spin-product functions for two protons consist of three that are symmetric ($\alpha\alpha, \beta\beta, \alpha\beta + \beta\alpha$) and one that is antisymmetric ($\alpha\beta - \beta\alpha$) where α and β are the functions corresponding to M_I values of +1/2 and -1/2 Thus it follows that for C_2H_2, g_I is 1 for even J, 3 for odd

J and the P and R branch lines will alternate in intensity. For C_2D_2, with spin functions α, β and γ representing the M_I values of +1, 0, -1, there are 6 symmetric nuclear spin combinations and three that are antisymmetric to exchange (can you write these?). Consequently the *even J* rotational lines are stronger in this case. The experimental observation of such intensity alternations confirms the D_h symmetry of acetylene, and in the present experiment serves as a useful check on the assignment of the J values for the P and R branch transitions.

Activity B

1. Show the relationship between the intensity of a spectral line and the population of the initial state.
2. Explain what you understand by isotope effect in vibrational and rotational spectroscopy.

4.0 Conclusion

Vibrational -rotational spectroscopy is the result of simultaneous rotation and vibration in gas molecules.

5.0 Summary

In this unit, we have learnt that;

a) High-resolution gas-phase IR spectra show information about the vibrational and rotational behavior of heteronuclear diatomic molecules.

b) The difference in energy, and thus the separation between adjacent lines (of the same isotope) in each branch of the IR spectrum, is related to B_e.

c) From the vibrational frequencies of the normal modes one can calculate the force constants for the different bond stretches and angle bends in the molecule.

6.0 Tutor marked assignment

1. Explain the vibrational and rotational transitions of polyatomic molecules.
2. From the vibrational frequencies of the normal modes calculate the force constants for the different bond stretches and angle bends in the C_2H_2 molecule.

7.0 Further reading and references

Atkins, P. W. (1982). Physical Chemistry, (2nd ed.), Oxford, Oxford University Press.

Atkins, P. W. (1982). Physical Chemistry, (3rd ed.), New York, Freeman.

Barrow, G. M. (1982). Physical Chemistry (4th ed.), Auckland, McGraw-Hill.

Ghersetti, S. and Rao, K. N. (1968). *Journal of Molecular Spectroscopy*. **28,** 27.

Ghersetti, S., Pliva, J. and K. N. Rao, (1971) *Journal of Molecular Spectroscopy* **38,** 53.

Harris, D. C. and Bertolucci, M. C. (1978). Symmetry and Spectroscopy, New York, Oxford University Press.

Herzberg, G. (1945) “Molecular Spectra and Molecular Structure 11. Infrared and Raman Spectra of Polyatomic Molecules," Princeton, N.J., Van Nostrand.

Hollas, J. M. (1987) "Modern Spectroscopy," New York, Wiley,.

Kostyk, E. and Welsh, H. L. (1980). *Can. J. Phys.* **58,** 534.

Kostyk, E. and Welsh, H. L. (1980) *Phys.* **58,** 912.

Levine, N. (1975). "Molecular Spectroscopy," New York, Wiley Interscience,.

NIST, (2009). *Electronic Spectroscopy*. Retrieved August 2, 2009 from Department of Chemistry and Biochemistry, National Institute of Standards and Technology (NIST) website: http://webbook.nist.gov/chemistry

Palmer, K. F., Mickelson, M. E. and Rao, K. N. (1972) *Journal of Molecular Spectroscopy* **44,** 131.

Steinfeld, J. (1978). "Molecules and Radiation," Cambridge, Mass., MIT Press.

Wilson, E. B., Decius, J. C and Cross, P. C. (1955) "Molecular Vibrations," New York, McGraw-Hill.(reprinted in unabridged form by Dover, New York (1980)).

Module 4: Theory of molecular spectroscopy

Unit 4 : Electronic spectroscopy

Contents

1.0 Introduction 298

2.0 Objectives 298

3.0 Definition of electronic spectroscopy 299

  3.1 Electronic excited states imply vibrational excitation 300

  3.2 Electronic excitations occur vertically on the potential energy curve/surface: the *Franck-Condon Principle*..301

  3.3 Electronic transitions and franck-condon factors..302

  3.4 Physical significance of the ranck-Condon factor 304

4.0 Conclusion 308

5.0 Summary 308

6.0 Tutor marked assignment 308

7.0 Further reading and references..309

1.0 Introduction

The energies involved when molecules make transitions by changing their electronic distributions are of the order of several electron volts and so the photons emitted or absorbed lie in the visible and ultraviolet regions of the electromagnetic spectrum. Electronic spectra give information about the electronic structures of molecules, and by analyzing them we are able to deduce the energies of electrons in different molecular orbitals and therefore to test the theories of molecular structure.

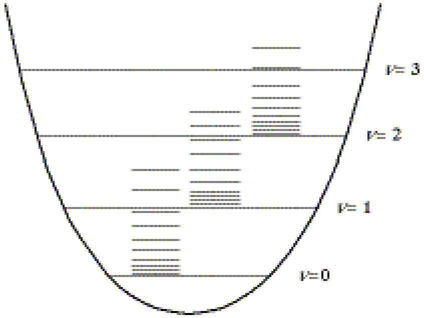
2.0 Objectives

By the end of this Unit, you should be able to:

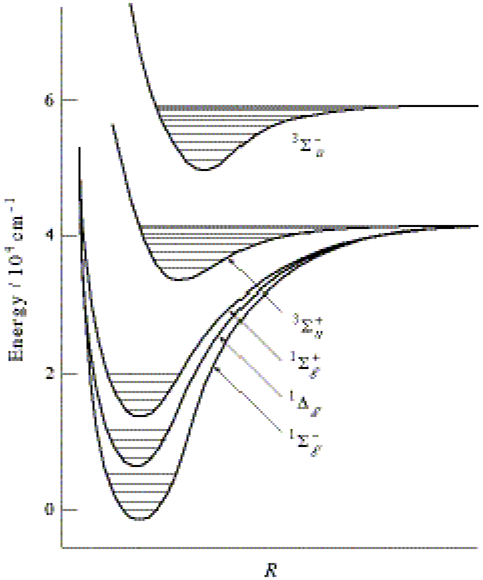
a) define Electronic spectroscopy;
b) explain the theory of Electronic spectroscopy;
c) explain Franck-Condon Principlea and
d) Use Franck-Condon Principle to account for the vibrational structure of electronic transitions.

3.0 Definition of Electronic Spectroscopy

If the electron arrangement in a molecule changes, then the energy of the molecule is generally changed. The spectra due to transitions between molecular states that differ in electron arrangement are called electronic spectra. The ro-vibrational picture using the Harmonic Oscillator (with corrections for anharmonicity) and Rigid Rotor (with corrections for rotation-vibration coupling and centrifugal distortion) is an excellent description for the ground state of a diatomic molecule (NIST, 2009).



In general, polyatomic molecules will have 3N-6 vibrational modes, and be asymmetric rotors with three different inertial axes I_A, I_B, and I_C. For each of the 3N-6 normal coordinate vibrations, a potential well will exist with a rotational energy level ladder that resembles the picture at left from McQuarrie & Simon. Each electronic state has its own ro-vibrational potential energy curve (diatomic)/surface (polyatomic).The anhamonic potential describing the ro-vibrational dynamics of a molecule is in general different for each electronic state. Excitation of a bound electron from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) increases the spatial extent of the electron distribution, making the total electron density larger and more diffuse, and often more polarizable. Thus, in a diatomic, one finds that the bond strength between the two atoms is weaker.



A slightly weaker bond means that the force constant for vibrations will be lower, and the relation between the force constant and the second derivative of the potential V, $k = \frac{d^2 V}{dx^2}$ indicates that the weaker force constant in the excited state implies not only a lower vibrational frequency, but simultaneously a broader spatial extent for the potential energy curve. This is illustrated in the figure at right:

Note that the highest lying state is well above the dissociation threshold. If this particular electronic state for a diatomic molecule were populated (by absorption of an energetic photon, or energetic collision with another high energy particle) then the molecule would dissociate.

Activity A

a) Define Electronic spectroscopy.

b) Explain the theory of Electronic spectroscopy.

3.1 Electronic excited states imply vibrational excitation

Another quite important feature to note is that the centers of each potential well are not aligned vertically. As explained below, this is why we have electronic transitions to different vibrational quantum numbers. By analogy to the situation where a vibrational excited state of a molecule must also contain rotational excitation, electronic excited states of molecules must also be vibrationally excited.

3.2 Electronic excitations occur vertically on the potential energy curve/surface: the *Franck-Condon Principle*

The Born-Oppenheimer approximation is based on the fact that the proton or neutron mass is roughly 1,870 times that of an electron, and that though nuclei move rapidly on a human time scale, the electrons move about 1,850 times faster. Thus, electronic motions when viewed from the perspective of the nuclear coordinates occur as if the nuclei were fixed in place. One can say that the electrons adiabatically, (or smoothly and continuously) follow the nuclei.

Applying the Born-Oppenheimer approximation to transitions between electronic energy levels led James Franck and R. Condon to formulate the ***Franck-Condon Principle***, which states that:

an obvious first question might be: When a stable ground state molecule absorbs ultraviolet/visible light, it may undergo excitation from its *HOMO* to an excited state such as the *LUMO*. The main effect is that the electronic configuration of the molecule will have changed on excitation, so that the bonding properties of the molecule will have just changed. Therefore, the nuclei must move to reorganize to the new electronic configuration, which instantaneously sets up a molecular vibration. This is why electronic transitions cannot occur in the absence of vibrational dynamics.

Elementary chemical reactions are a much more complex version of electronic transitions, and the nuclei of all products (and surrounding solvent, if a solution reaction) must reorganize around the new electronic configuration. This is why vibrational dynamics are an excellent way to study fundamental reaction dynamics processes, and why a Nobel Prize was awarded in 1999 to Prof. A. Zewail for the study of chemical reaction dynamics; he and his many co-workers showed that the complex interplay between electronic transitions and molecular vibrations can provide a real-time movie of chemical reactions as they occur.

3.3 Electronic Transitions and Franck-Condon Factors

If a transition between molecular quantum states is to be stimulated by absorption or emission of light, the *transition dipole moment* must be non-zero. To explain the *Franck-Condon Principle* more mathematically, we can calculate the *transition dipole matrix elements* $\mu_{fi} = \langle \Psi_f | \mu | \Psi_i \rangle$. To simplify a very complicated problem as much as possible, we will discuss only a diatomic molecule for the time being. For electronic energy levels, the total wavefunction is a separable product of four kinds of motion:

- ***Nuclear*** (with electrons following the nuclear displacements...)
- ***Translational***
- ***Rotational***
- ***Vibrational***
- ***Electronic*** (with nuclei immobile on the relevant time scales for motion, *via* the B.-O. approximation)

The wavefunctions must be written as a product of each of the four component wavefunctions. The translational wavefunctions for the molecule are given by particle-in-a-box eigenfunctions. Rotational dynamics are described by the *Rigid Rotor* wavefunctions with corrections for bond length changes caused by vibrational excitations (*i.e.*, rotation-vibration coupling) and with corrections for *centrifugal distortion* if the molecule is highly excited rotationally. Vibrational dynamics are described by *Harmonic Oscillator* wavefunctions with corrections for anharmonicity. The electronic wavefunctions given by the relevant molecular orbitals describing the ground or excited electronic states. Thus, the overall wavefunction for a diatomic molecule must be written as:

$$\Psi_{total} = \Psi_{trans} \times \Psi_{rot} \times \Psi_{vib} \times \Psi_{electr}$$

To describe the Franck-Condon factors, we will simplify the problem by considering only the largest energy parts of the problem, which are the last two terms: the vibrational and electronic energy.Thus, though the true statement of the *Franck-Condon Principle* is given by $\langle \Psi_{total,\ final} | \hat{\mu} | \Psi_{total,\ initial} \rangle$, we will instead consider the simpler case of

$$\langle \Psi_{electr,\ vib,\ final} | \hat{\mu} | \Psi_{electr,\ vib,\ initial} \rangle \quad where \quad \Psi_{electr,\ vib,\ i} = \Psi_{elect,\ i} \times \Psi_{vib,\ i}$$

In this case, we must consider the total molecular dipole for the operator $\hat{\mu}$, now including the charges and positions of both electrons and nuclei:

$$\hat{\boldsymbol{\mu}} = -e \sum_i \boldsymbol{r}_i + e \sum_i Z_i \boldsymbol{R}_i$$

where $\boldsymbol{r_i}$ are the electronic coordinates, $\boldsymbol{Z_i}$ are the nuclear charges, and $\boldsymbol{R_i}$ are the nuclear coordinates.

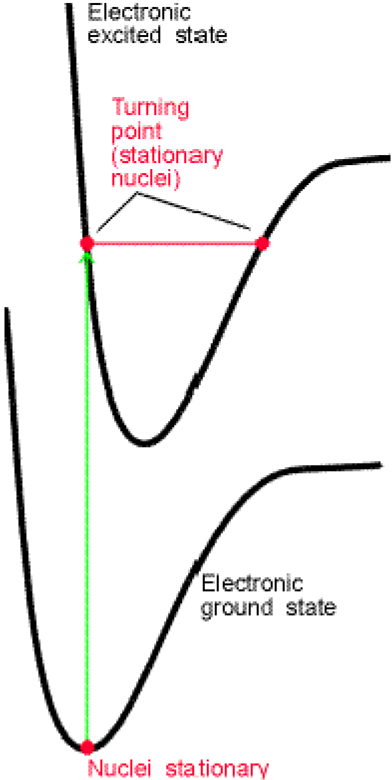
Now the problem of stating the ***Franck-Condon Principle*** mathematically is to evaluate

$$\begin{aligned} &\langle \Psi_{elect,\ final} \times \Psi_{vib,\ final} | \left(-e \sum_i \boldsymbol{r}_i + e \sum_i Z_i \boldsymbol{R}_i\right) | \Psi_{elect,\ initial} \times \Psi_{vib,\ initial} \rangle \\ &= \langle \Psi_{elect,\ final} | -e \sum_i \boldsymbol{r}_i | \Psi_{elect,\ initial} \rangle \times \langle \Psi_{vib,\ final} | \Psi_{vib,\ initial} \rangle + e \sum_i Z_i \ \langle \Psi_{electr,\ final} | \Psi_{electr,\ initial} \rangle \times \langle \Psi_{vib,\ final} | \boldsymbol{R}_i | \Psi_{vib,\ initial} \rangle \end{aligned}$$

.

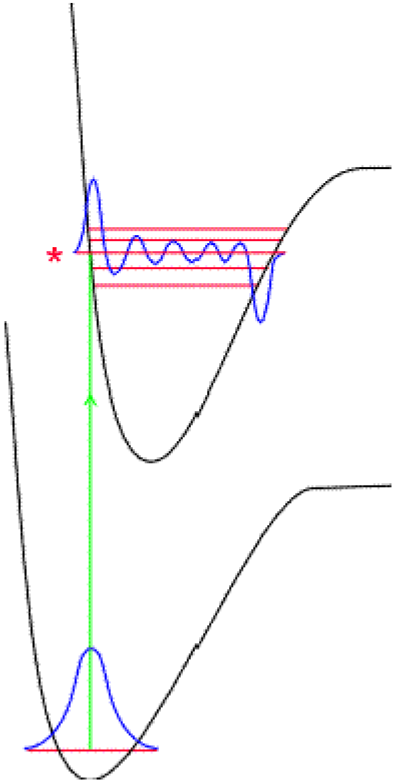
The Born-Oppenheimer approximation tells us that the nuclear coordinate wavefunction for the vibrations, $\Psi_{vib,\ i}$, factors out from the first term (*via the B.-O.* approximation) because the nuclei (that are vibrating) are moving so much more slowly than the electrons. The second term on the right-hand side of the equation must be identically zero, because the overlap between different electronic states is zero because of orthogonality. Thus, the ***Franck-Condon Principle*** can now be written as

$$
\begin{aligned}
\langle \Psi_{electr,\,vib,\,final} | \hat{\mu} | \Psi_{electr,\,vib\,initial} \rangle &= \langle \Psi_{elect,\,final} | -e \sum_i \boldsymbol{r}_i | \Psi_{elect\,initial} \rangle \times \langle \Psi_{vib\,final} | \Psi_{vib\,initial} \rangle \\
&= -e \sum_i \text{¿} \langle \Psi_{electr,\,final} | \boldsymbol{r}_i | \Psi_{electr\,initial} \rangle \times \langle \Psi_{vib\,final} | \Psi_{vib\,initial} \rangle \\
&= \boldsymbol{\mu}_{electr,\,final\,initial} \times \boldsymbol{S}(vib,\,final,\,initial) \\
where\ \ \boldsymbol{S}(vib,\,final,\,initial) &= \langle \Psi_{vib\,final} | \Psi_{vib\,initial} \rangle \\
&\text{is defined as the } \textbf{Franck-Condon factor.}
\end{aligned}
$$



3.4 Physical Significance of the Franck-Condon factor

Source: NIST

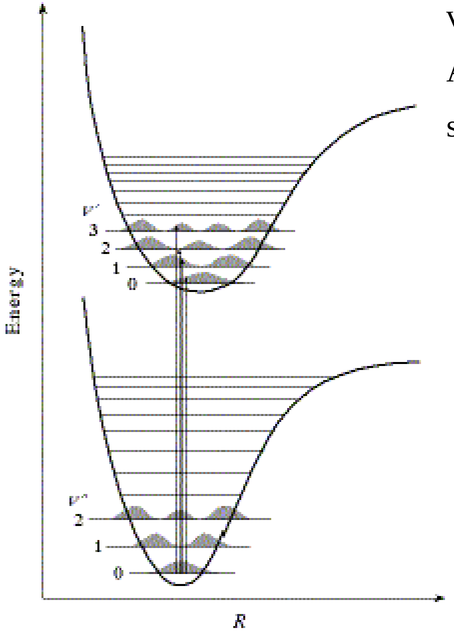


The ***Franck-Condon factor*** determines the probability for electronic transitions, and thus determines the intensity of spectral lines. To have a large ***absorption cross section***, or high probability that the molecule will absorb/emit UV-visible light, then there must be large overlap between the vibrational states in the initial and final electronic states. The case when good overlap is obtained is illustrated in the figure at right.

The ground, or initial state will most often be in the $v = 0$ vibrational level, since the vibrational energy will normally be 1,000-3000 cm^{-1}, many times the thermal energy kT, which at room temperature is about 200 cm^{-1}.

The most probable position for which the transition can occur is from the equilibrium bond distance for a diatomic molecule, R_e, since with only zero-point vibrations occurring, the vibrational wavefunction is a symmetric *even* function with no nodes.

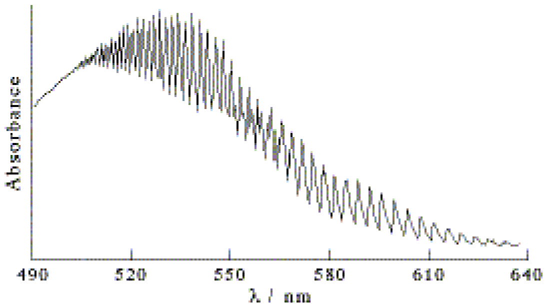
Since the *Franck-Condon* principle tells us that the electronic transitions occur with no immediate motion of the nuclei, the excited state ***at the moment of creation*** is not vibrating. Thus, the probability for creation of an electronic excited state will be maximized if the excited state vibrational wavefunction is located vertically above the ground state potential energy curve so as to make creation of the excited state occur at a *classical turning point* where the molecule is as compressed as can be compatible with the excited state vibrational wavefunction. This is illustrated in the figure to the left. In the example shown at right (both from Atkins) it appears that the electronic transition occurs from v=0 in the ground state to v' ~ 9 in the excited state.



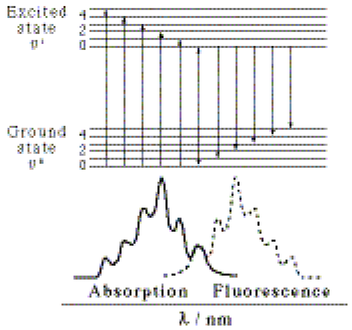
Vibronic Progressions Demonstrate How Electronic Spectra Involve Many Vibrational Levels. Source: NIST

Electronic transitions are possible for a wide range of vibrational levels within the initial and final electronic states. We refer to combination of vibrational and electronic quantum states as the molecular **vibronic manifold**. An example of how the ground electronic state, with v=0 can have non-zero overlap with the excited electronic state vibrational levels is shown in the figure at left from McQuarrie and Simon.

In certain ultra-high resolution spectroscopies, such as molecular beam free-jet expansions, the molecules become cooled to temperatures near zero Kelvin. Under these conditions, the individual rotational levels within the vibronic manifold become resolvable, and one observes the **ro-vibronic transitions**. An example of the **vibronic progression** for the electronic and vibrational absorption spectrum of molecular iodine (I_2) is shown below.



A medium sized molecule often has absorption fluorescence resembling those below, with absorption the solid line on the left, and fluorescence emission the dashed line on the right. In the energy diagram at the top of the figure, the energies for transitions from the ground electronic state occur from the $v = 0$ vibrational level. The ground electronic state for most neutral organic species will have a singlet configuration, and is denoted S_0 to indicate that it is a ground state. When we resolve the vibronic manifold as in the figures above and below, we add the vibrational quantum number to the state description, now called $S_{0,v=0}$. The excitations shown are for the transitions $S_{1,v=4} <= S_{0,v=0}$ down to $S_{1,v=0} <= S_{0,v=0}$. The latter transition is often called the '**0-0**' transition, since it occurs between the $v=0$ vibrational levels, and is the lowest energy excited state.



Kasha's Rule proposed by Prof. Michael Kasha in 1953 states that emission will always occur from the $S_{1,v=0}$ state. In the next section, we will discuss the rapid energy flow that occurs to funnel excitations from any higher-lying excited states to the $S_{1,v=0}$ state, principally ***vibrational relaxation*** and ***internal conversion***. ***Kasha's Rule*** explains the mirror image symmetry between the vibronic structure of the stimulated absorption and spontaneous emission transitions (NIST, 2009).

Activity B

a) State the kinds of motion responsible for total wavefunction of electronic energy levels.

b) Explain the physical significance of the Franck-Condon factor

4.0 Conclusion

Electronic spectra give information about the electronic structures of molecules, and by analyzing them we are able to deduce the energies of electrons in different molecular orbitals and therefore to test the theories of molecular structure.

5.0 Summary

In this unit, we have learnt that;

(i) the spectra due to transitions between molecular states that differ in electron arrangement are called electronic spectra.

(ii) if a transition between molecular quantum states is to be stimulated by absorption or emission of light, the *transition dipole moment* must be non-zero and

(iii) for electronic energy levels, the total wavefunction is a separable product of four kinds of motion.

6.0 Tutor marked assignment

1. explain Franck-Condon Principle;
2. use Franck-Condon Principle to account for the vibrational structure of electronic transitions.

7.0 Further reading and references

Atkins, P. W. (1982). Physical Chemistry, (2nd ed.), Oxford, Oxford University Press.

Atkins, P. W. (1982). Physical Chemistry, (3rd ed.), New York, Freeman.

Barrow, G. M. (1982). Physical Chemistry (4th ed.), Auckland, McGraw-Hill.

Ghersetti, S. and Rao, K. N. (1968). *Journal of Molecular Spectroscopy*. **28,** 27.

Ghersetti, S., Pliva, J. and K. N. Rao, (1971) *Journal of Molecular Spectroscopy* **38,** 53.

Harris, D. C. and Bertolucci, M. C. (1978). Symmetry and Spectroscopy, New York, Oxford University Press.

Herzberg, G. (1945) “Molecular Spectra and Molecular Structure 11. Infrared and Raman Spectra of Polyatomic Molecules," Princeton, N.J., Van Nostrand.

Hollas, J. M. (1987) "Modern Spectroscopy," New York, Wiley,.

Kostyk, E. and Welsh, H. L. (1980). *Can. J. Phys.* **58,** 534.

Kostyk, E. and Welsh, H. L. (1980) *Phys.* **58,** 912.

Levine, N. (1975). "Molecular Spectroscopy," New York, Wiley Interscience,.

NIST, (2009) *Electronic Spectroscopy*. Retrieved August 2, 2009 from Department of Chemistry and Biochemistry, National Institute of Standards and Technology (NIST) website: http://webbook.nist.gov/chemistry

Palmer, K. F., Mickelson, M. E. and Rao, K. N. (1972) *Journal of Molecular Spectroscopy* **44,** 131.

Steinfeld, J. (1978). "Molecules and Radiation," Cambridge, Mass., MIT Press.

Wilson, E. B., Decius, J. C and Cross, P. C. (1955) "Molecular Vibrations," New York, McGraw-Hill.(reprinted in unabridged form by Dover, New York (1980)).

Module 4: Theory of molecular spectroscopy

Unit 5: Introduction to symmetry

Contents

1.0 Introduction 312

2.0 Objectives 313

3.0 Definition of symmetry 314

  3.1 Symmetry elements and operations 314

4.0 Conclusion 321

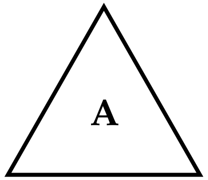
5.0 Summary 321

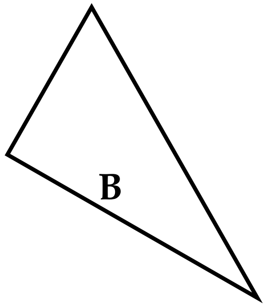
6.0 Tutor marked sssignment 321

7.0 Further reading and other resources 322

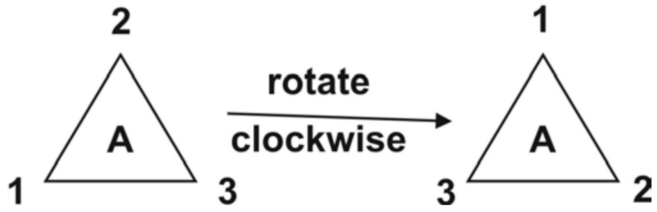
1.0 Introduction

The idea of symmetry is a familiar one: we speak of a shape as “being symmetrical”, “unsymmetrical” or even more symmetrical than some other shapes”. Scientifically, we need to specify ideas to symmetry in a more quantitative way. Which of these shapes will you say is more symmetrical?





If you rotate a piece of cardboard shaped like “A” by one third of a turn, the result looks the same as the starting point.



Since the two structures above are indistinguishable, we say that the rotation is a symmetry operation of the shape.

2.0 Objectives

By the end of this unit, you should be able to:

(a) define symmetry elements and symmetry operations and

(b) detect the presence of an axis of symmetry, plane of symmetry, centre of symmetry, and an axis of improper rotation in a body.

3.0 Definition of symmetry

An object is said to be symmetrical if on operated upon either by rotation or reflection on a plane, or inversion through the centre remains indistinguishable. This operation consists of treating the plane as a mirror, which gives an image behind the mirror that is identical to the scene in front of the mirror. This reflection in the mirror produces a result that is indistinguishable from that existing originally (Atkins,1982; Babarinde, 2008 & Barrow, 1982). The reflection process is an example of a symmetry operation. It is the symmetry operation associated with a plane of symmetry. The plane of symmetry is an example of an element of symmetry. In formal terms, we say that an object is *symmetric* with respect to a given mathematical operation, if when applied to the object, this operation does not change the object or its appearance. Two objects are symmetric to each other with respect to a given group of operations if one is obtained from the other by some of the operations (and vice versa). Symmetries may also be found in living organisms including humans and other animals.

3.1 Symmetry elements and operations

Each symmetry element will generate symmetry operation. The operations that will be generated are as tabulated below.

3.1.1 Identify (E): Does nothing, it has no effect. All molecules/objects possess the identity operation, that is, posses E. E has the same importance as the number 1 does in multiplication (*E* coming from the German word “Einheit”, meaning unity). E is needed in order to define inverses.

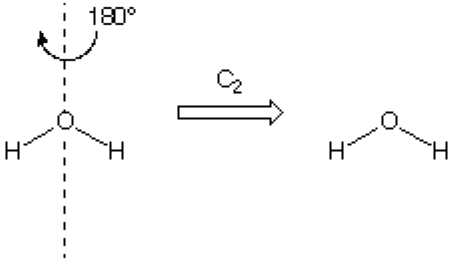
3.1.2 Proper axis of rotation (C_n): Rotation through angle $\theta = 360^o/n$

C_2 = 180° rotation, C_3 = 120° rotation, C_4 = 90° rotation, C_5 = 72° rotation,

C_6 = 60° rotation, etc

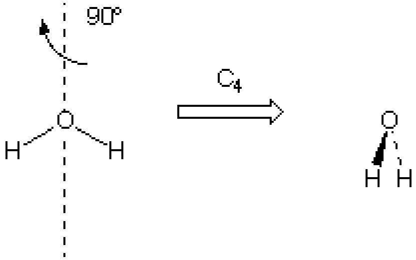
Rotation of H_2O about the axis shown by 180° (C_2) gives the same molecule back.

Therefore H_2O possess the C_2 symmetry element.



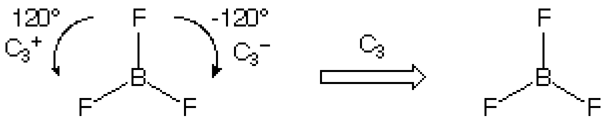
However, rotation by 90° about the same axis does not give back the identical molecule

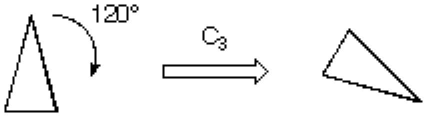
Therefore H_2O does NOT possess a C_4 symmetry axis.



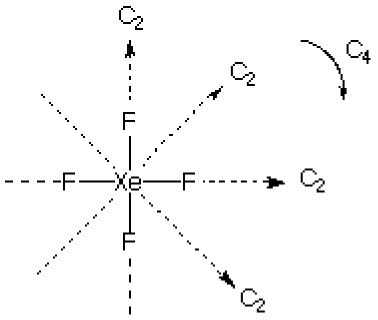
BF_3 posses a C_3 rotation axis of symmetry.

In each case both directions of rotation must be considered.





This triangle does not posses a C_3 rotation axis of symmetry.

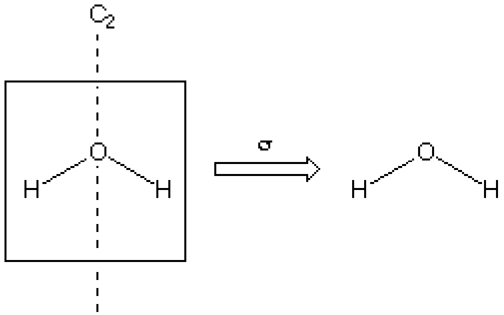


XeF_4 is square planar. It has four different C_2 axes. It also has a C_4 axis coming out of the page called the principle axis because it has the largest n.

By convention, the principle axis is in the z-direction.

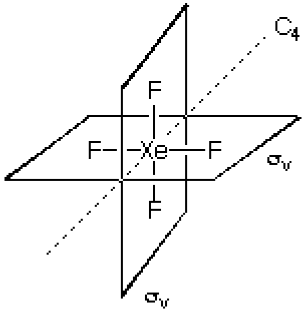
When there is more than one axis in a molecule, one of them is the principal axis which has the largest value of n. The principal axis is perpendicular to the plane of the molecule. When there is only one axis of rotation that axis constitutes the principal axis. For an equilateral triangle there are $2C_3$ and $3C_2$ axes. Since 3 is greater than 2 then the principal axis is C_3.

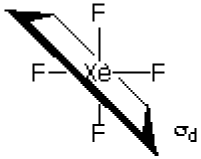
3.1.3 Mirror plane (σ): Reflection through plane. If reflection about a mirror plane gives the same molecule/object back than there is a plane of symmetry (σ). If plane contains the principle rotation axis (i.e., parallel), it is a vertical plane (σ_v).If plane is perpendicular to the principle rotation axis, it is a horizontal plane (σ_h). If plane is parallel to the principle rotation axis, but bisects angle between 2 C_2 axes, it is a diagonal plane (σ_d). H_2O posses 2 σ_v mirror planes of symmetry because they are both parallel to the principle rotation axis (C_2).

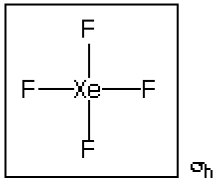


XeF_4 has two planes of symmetry parallel to the principle rotation axis: σ_v

XeF_4 has two planes of symmetry parallel to the principle rotation axis and bisecting the angle between 2 C_2 axes : σ_d . XeF_4 has one plane of symmetry perpendicular to the principle rotation axis: σ_h



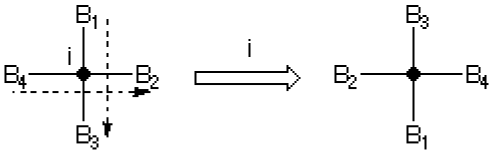




The mirror plane that is perpendicular to the principal axis is the horizontal plane (σ_h). The mirror plane that is parallel to the principal axis is the vertical plane (σ_v). The plane that bisects the opposite angles of a square and also parallel to the principal axis in the dihedral plane (σ_d).

3.1.4 Inversion (i): Inversion through the centre.

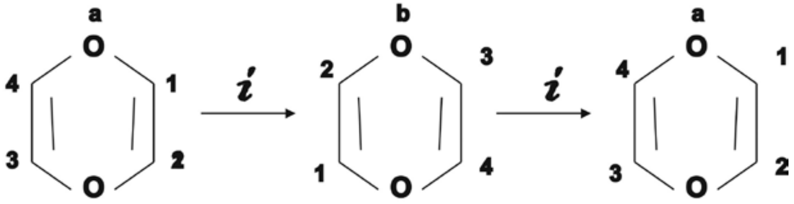
The element that corresponds to this operation is a center of symmetry or inversion center. The operation is to move every atom in the molecule in a straight line through the inversion center to the opposite side of the molecule.



Therefore XeF_4 posses an inversion center at the Xe atom.

When there are two inversions then the result will be the identity (E).

$$\iota^2 = E$$



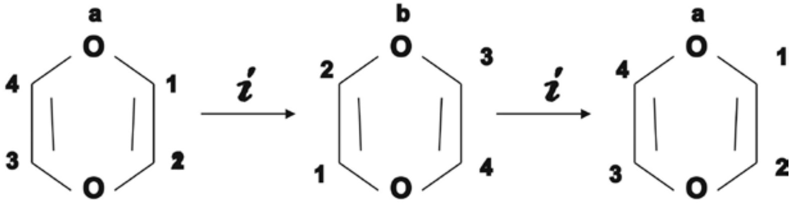
3.1.5 Improper axis of rotation (S_n): Rotation through axis C_n followed by reflection in a plane. There is n-fold rotation followed by reflection through mirror plane perpendicular to rotation axis. A body such as equilateral triangle has improper axis of rotation S_n. It can be rotated through C_3 at the centre of the triangle and there is also a plane on the paper. The principal axis C_3 is perpendicular to the plane of the paper. A combination of the proper axis of rotation and the mirror plane gives the improper axis of rotation S_n.

$$S_3 = \sigma_h C_3$$

Conventionally, the right hand side of the above equation is read as proper rotation C_3 followed by mirror plane σ_h.

When there are two inversions then the result will be the identity (E).

$$\iota^2 = E$$



For invention: i^n = i when n is odd.

i^n = E when n is even.

Reflection twice produces the identity.

$\sigma^n = \sigma$ when n is odd.

$\sigma^n = E$ when n is even.

Activity A

(a) define symmetry elements and symmetry operations and

(b) identify all the symmetry elements in XeF_4

4.0 Conclusion

As various examples suggest, we can describe the symmetry of a molecule in terms of the elements of symmetry of the molecule.

5.0 Summary

In this unit we have learnt that:

(i) that a molecule has any particular element of symmetry can be checked by carrying out the symmetry operation associated with each symmetry element.

(ii) if the operation does nothing more than leave the positions of atoms unchanged or carries one atom of a set of identical atoms into a position of another atom of the set, the result will be indistinguishable from the existing initially.

(iii) when this is the result of the symmetry operation, the molecule does indeed have the corresponding symmetry elements and

(iv) the symmetry elements that any molecule can possess are E, C_n, σ, I, and S_n.

6.0 Tutor marked assignment

(i) determine the symmetry elements in the following : (a) Ammonia (b) A rectangular sheet of paper (c) Water.

(ii) determine the number of planes of symmetry in each of the following: (a) $SOCl_2$ (b) NH_3(c) H_2S

7.0 Further reading and other resources

Atkins, P. W. (1982). Physical Chemistry, (2nd ed.), Oxford, Oxford University Press.

Babarinde, A. (2008). Introduction to Symmetry and Group Theory, (1st ed.), Ijebu-Ode, Luck Odoni.

Barrow, G. M. (1982). Physical Chemistry (4th ed.), Auckland, McGraw-Hill.

Module 4: Theory of molecular spectroscopy

Unit 6: Application of symmetry and group theory

Contents

1.0 Introduction 325

2.0 Objectives........ 325

3.0 Determination ofpoint groups........ 325

- 3.1 Conditions for the formation of a symmetry point group 326

- 3.2 Classification of the symmetry of molecules........ 327

- 3.2 Point Group determination chart 329

3.3 Identification of symmetry elements in a molecule 334

3.4 Symmetry in crystal structures 335

3.5 Implication of symmetry on properties of molecules 340

4.0 Conclusion 341

5.0 Summary 341

6.0 Tutor marked assignment 342

7.0 Further reading and other resources 16

1.0 Introduction

The key to applying Group Theory is to be able to identify the "Point”. The possible Symmetry Operations associated with a molecule are determined by the Symmetry Elements possessed by that molecule. Therefore the first step in applying Group Theory to molecular properties is to identify the complete set of Symmetry elements possessed by the molecule. This requires the individual to visually identify the elements of symmetry in a 3-dimensional object.

2.0 Objectives

By the end of this Unit, you should be able to:

(c) classify molecules according to their point group symmetry;

(d) use the knowledge of symmetry of a molecule deduce whether it can be polar or optically active;

(e) state the group property and

(f) determine the properties of molecules using their symmetry.

3.0 Determination of point groups

The H_2O molecule, for example, has the symmetry elements E, C_2, σ_v and σ_v^1. It should be noted that there is no σ_h for H_2O because the planes present are parallel to the principal axis C_2. The sets of symmetry operations associated with such collections of symmetry elements are referred to as point groups. The adjective “point” is used because the symmetry operations associated with all the symmetry elements that are dealt with here leave a point of or in the molecule fixed in space (Babarinde, 2008).

Each collection of symmetry operations constitutes a point group, and each point group is given a symbol. The symbol usually written in bold face type is based on the principal elements of symmetry of that point group. Group Theory is one of the most powerful mathematical tools used in Quantum Chemistry and Spectroscopy. It allows the user to predict, interpret, rationalize, and often simplify complex theory and data.

At its heart is the fact that the set of operations associated with the symmetry elements of a molecule constitute a mathematical set called a Group. This allows the application of the mathematical theorems associated with such groups to the Symmetry Operations.

3.1 Conditions for the formation of a symmetry point group

1. Any result of two or more operations must produce the same result as application of one operation within the group, that is, the group multiplication table must be closed for example, H_2O, which has E, C_2 and 2 σ_v's. The group multiplication table obtained is presented below. The table is closed, that is, the result of two operations produces an operation in the group.

	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v

σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

2. must have an identity ($\hat{E}$)

3. all elements must have an inverse, that is, for a given operation ($\hat{A}$) there must exist an operation ($\hat{B}$) such that $\hat{A}\hat{B}=\hat{E}$

3.2 Classification of the symmetry of molecules

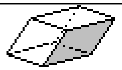
Certain symmetry operations can be present simultaneously, while others cannot.

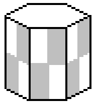
There are certain combinations of symmetry operations, which can occur together.

Symmetry groups contain elements and there mathematical operations.

For example, one of the symmetry elements of H_2O is a C_2-axis. The corresponding operation is rotation of the molecule by 180° about an axis.

Table 4.6.1: Properties of symmetry point groups

Point group	Properties	Example
C_1	E	

C_i	E + i	
C_s	E + σ	NOCl
C_n	C_n= E +C_n	H_2O_2 (C_2)
C_{nv}	$E + C_n + n\sigma_v$	H_2O(C_{2v})
C_{nh}	$E + C_n + \sigma_h$	**Trans-$C_2H_2Cl_2$ (C_{2h})**
D_{nd}	$E + C_n + nC_2 \perp C_n + n\sigma_d$	Cyclohexane (D_{6h})
D_n	$E + C_n + nC_2 \perp C_n$	 D_6

D_{nh}	$E + C_n + nC_2 \perp C_n + \sigma_h$	Benzene (D_{6h})
$C_{\infty v}$	Heteronuclear diatomic	HCl
$D_{\infty h}$	homonuclear diatomic	H_2
T_d	Tetrahedral structures	CH_4
O_h	Octahedral structures	SF_6
R_3	Spherical structures	Sphere

Source: Babarinde, 2008

3.2 Point Group Determination Chart

The flow chart bellow gives the steps to the determination of point groups for different molecules .

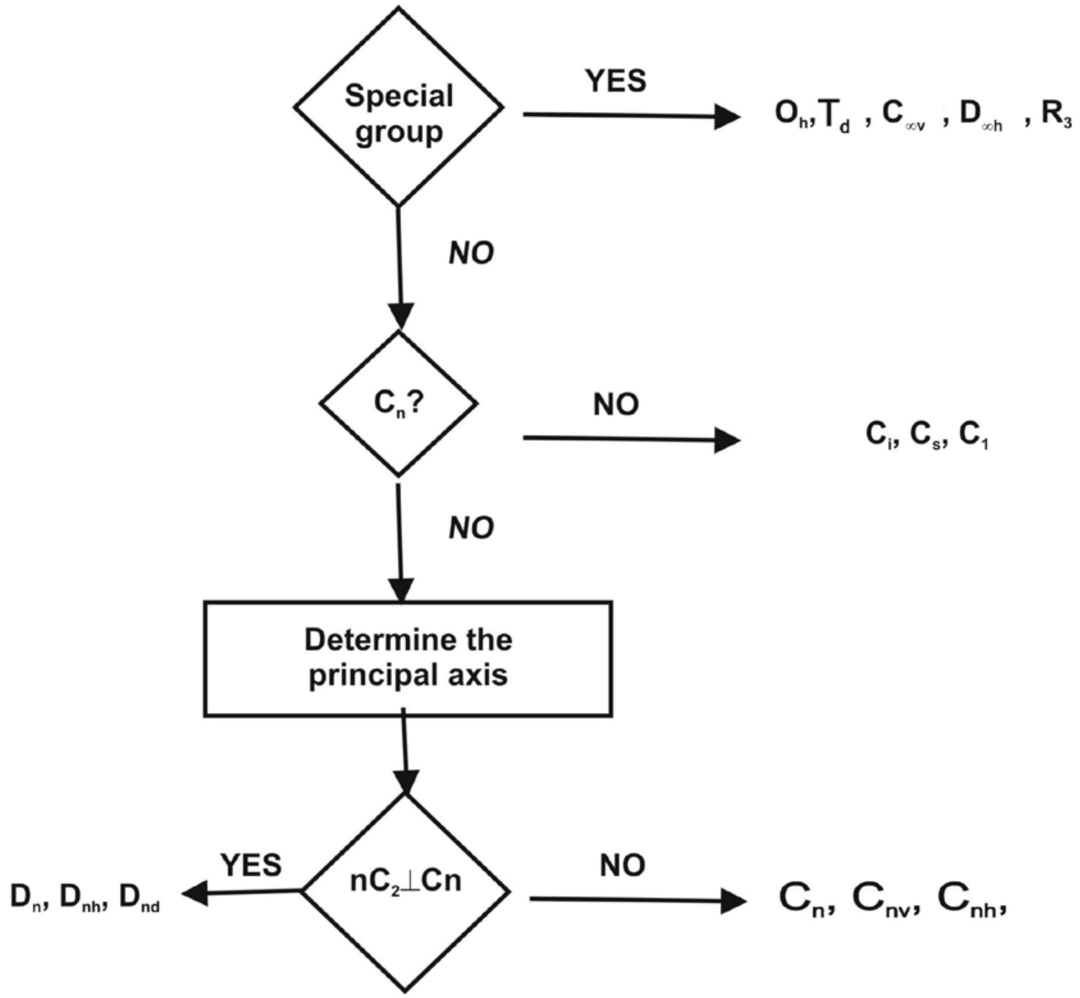

Special group
YES
O_h, T_d, C_∞v, D_∞h, R_3
NO
C_n?
NO
C_i, C_s, C_1
NO
Determine the principal axis
nC_2⊥Cn
YES
D_n, D_nh, D_nd
NO
C_n, C_nv, C_nh,

Figure 4.6.1: Condensed flow chart for the determination of point groups in molecules.

Source: Babarinde, 2008

Activity A

1. List all the symmetry elements that a molecule can possess.
2. Determine the symmetry elements in the following molecules and hence their point groups: (i) $Ni(CN)_4$ (ii) BF_3 (iii) NH_3 (iv) C_6H_6 (v) C_6H_{12}

Examples:

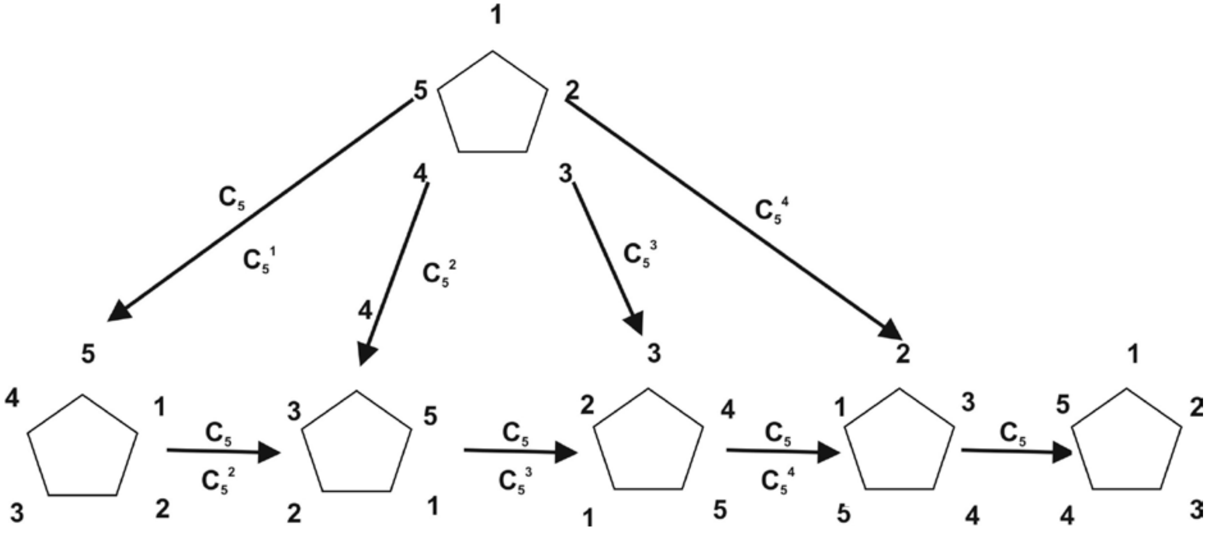
1. Suppose we now rotate an equilateral triangle by half a turn about an axis through a vertex by turning it over.

How many operations of this type are possible?

Answer: Three, one through each vertex. We have now specified the first of our symmetry operations called proper rotation, which is given the symbol C. The symbol is given a subscript to indicate the order of the rotation. One third of a term is called C_3.

2. What operations are generated by a C_5 axis?

Ans: C_5, C_5^2, C_5^3, and C_5^4



Question: What happens if we go one stage further?

Answer: We get back to where we started. The shape now is identical with the starting point. We say that is C_5^5 and of course any $C_n^n = E$ where E is called the identity operation. It is the operation of doing nothing. Every object has this symmetry element.

Another symmetry operation is the plane of symmetry with symbol, σ(sigma). The element generate only one operation (σ^1) because σ^2 = E. Many molecules have one or more planes of symmetry. A flat molecular plane such as in H_2O gives σ as the plane of the molecule while another mirror plane σ^1 is at right angles to it and reflects one H atom to the other.

The water molecule can also be brought to an indistinguishable configuration by a simple rotation. Can you locate the proper rotation axis and what is the order?

Ans: A two-fold rotation axis, C_2.

Water molecule, therefore, has four symmetry elements. List them. E, σ, σ', C_2. Each of these elements generates only one operation, so the four symbols also describe the four operations.

The elements are E, C_2, σ and σ' while the symmetry operators are E, C_2, σ and σ'. Pyridine is another flat molecule, which is analogous to water.

The symmetry elements and operators are E, c_2, σ and σ'. Several molecules have this set of symmetry elements that it is convenient to classify them under one name, C_{2v}.

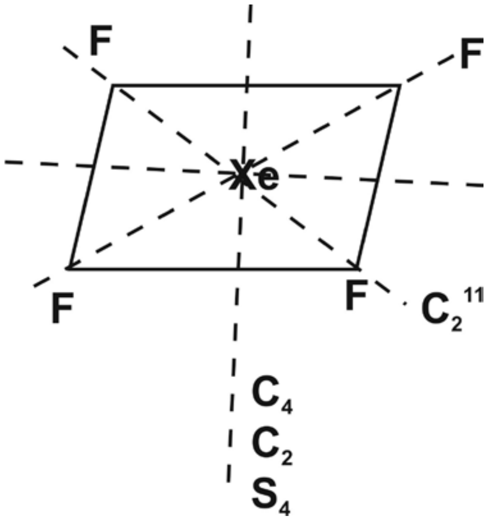
There is a simple restriction on planes of symmetry, which is rather obvious but can assist you in locating planes. A plane must either pass through an atom or else that type of atom must occur in pairs, and symmetrical too on either side of the plane.

Activity B

1. Show the steps to determining the point groups of different objects.

3.3 Identification of symmetry elements in a molecule

Some molecules have many symmetry elements, some of which are not immediately obvious as in X_eF_4.

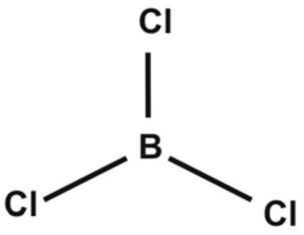


Hence the complete list of symmetry element is

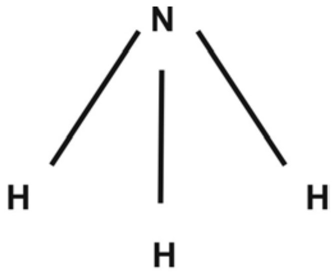
$$E, C_4, C_2, S_4, i, 2C_2', 2C_2'', \sigma_n, 2\sigma, 2\sigma' = D_{4h}$$

Examples: List the symmetry elements of the following molecules:

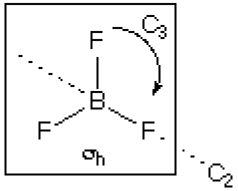
(i) BCl_3 (ii) NH_3 (iv) BF_3



$E, C_3, 3C_2\sigma_h, 3\sigma, S_3$



$2C_3; 3\sigma v; E$



3.4 Symmetry in crystal structures

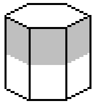
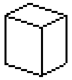
The X-ray analysis of crystals has shown that they are made up of simple units consisting of atoms, ions or molecules. Each crystal is just a repetition of the basic unit. Each crystal unit is called the unit cell, or space lattice. A crystal is a regular three-dimensional arrangement of the atoms, ions or molecules of which it is built up. The three-dimensional design of a crystal is composed of identical units forming a three-dimensional network of cells, which divide the space into equal volumes with no space excluded. This is only possible when the points are arranged in such a way that each of the points has exactly the same environments as any similar point in the system. These points with identical surroundings are referred to as lattice points while the three-dimensional arrays of such points are called space lattices.

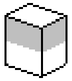
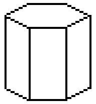
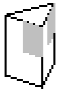
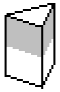
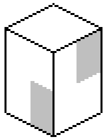
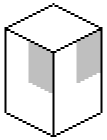
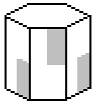
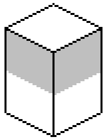
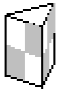
All crystals fall into any of the seven crystal systems; cubic, monoclinic, triclinic, orthorhombic, tetragonal, rhombohedral, and hexagonal. Generally, three imaginary lines are drawn between the centres of opposite faces to represent the three axes of symmetry. The system to which a crystal belongs depends on the relative lengths of the axes of symmetry and the angle at which the axes meet in the unit cell. Due to the regularity in the distribution of the points in a space lattice its essential geometry can be determined by three lattice vectors, called lattice constants (a, b, c). and the inter-axial angles ∀, ∃ and (. These lattice parameters describe the unit cell or the smallest repeating unit of lattice. A. In X-ray crystallography, the lattice constants are repeat distances along axes x, y, and z, respectively. They are referred to as axial ratios while the inter-axial angles ∀, ∃ and (are called axial angles. Bravais showed that there are only fourteen different ways in which lattice points can be arranged in a regular three-dimensional pattern.

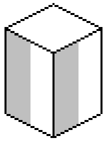
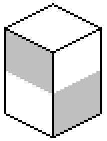
Table 4.6.2: The fourteen Bravais lattices of the seven crystal systems.

Serial number	System	Axes	Angle	Number of lattices
1	Cubic	a = b = c	∀ = ∃ = (= 90°	3
2	Monoclinic	a≠ b ≠ c	∀ = (= 90°≠∃	2
3	Triclinic	a ≠ b ≠ c	∀ ≠ ∃ ≠ (≠ 90°	1
4	Tetragonal	a = b≠ c	∀ = ∃ = (= 90°	2
5	Hexagonal	a = b≠ c	∀ = ∃ = 90°,(=120°	1
6	Rhombohedral	a = b = c	∀ = ∃ = (≠ 90°	1
7	Orthorhombic	a ≠ b ≠ c	∀ = ∃ = (= 90°	4

Table 4.6.3: Symmetry point groups of 3-Dimensional Solids. ***Source:*** **Newcastle (2009)**

S/N	3D UNIT CELL	POINT GROUP	S/N	3D UNIT CELL	POINT GROUP
1		C_1	9		C_{6v}
2		C_2	10		D_{2h}

3		C_{2v}	11		D_{6h}
4		C_3	12		C_i
5		C_{3v}	13		S_4
6		C_4	14		S_6
7		C_{4v}	15		D_3

		C_{4h}	16		D_{2d}

3.5 Implication of Symmetry on properties of molecules

There are immediate consequences of symmetry on properties of molecules. These are given below.

1. **Electric dipole moment** Only molecules belonging to the groups C_n, C_{nv} and C_s may have electric dipole moment. Out of the three point groups, C_n, and C_{nv} must have their electric dipole moment lying along the rotation axis. A molecule having a C_n axis cannot have a dipole moment perdicular to its axis but it may exis parallel to the axis. The same rule applies to C_{nv}.

2. **Optical activity**

The plane of a polarized light can only be rotated by a molecule if it cannot be superimposed on its mirror image. This implies that symmetry operation that should be looked for in order to determine the optical activity is the improper axis of rotation, S_n. If S_n is present, the object can be superimposed on its mirror image, hence cannot be optically active. On the other hand, absence of S_n implies that superposition is impossible, and optical activity may occur. It should be noted that any improper rotation axes that may be implied by the group must included. All the groups in C_{nh} have S_n concealed in them since they contain C_n and σ_h. In general, any point group having the centre of inversion, i, as a symmetry element also possesses S_n, where the minimum value of n is 2. It should be understood that an inversion can be regarded as a C_2 (180° rotation) followed by a σ_h. Consequently, any molecule with centre of inversion cannot be optically active. However, it is not all molecules with a centre of inversion that are optically active. For example, a molecule that has symmetry point group S_4 but has no centre of inversion shows optical activity (Atkins, 1982; Barrow, 1982).

Activity B

1. state the conditions for the formation of point group.
2. determine the number of planes of symmetry in each of the following:

   (i) $SOCl_2$ (ii) H_2S

4.0 Conclusion

As various examples suggest, we can describe the symmetry of a molecule in terms of the elements of symmetry of the molecule.

5.0 Summary

In this unit we have learnt that:

(i) that a molecule has any particular element of symmetry can be checked by carrying out the symmetry operation associated with each symmetry element;

(ii) if the operation does nothing more than leave the positions of atoms unchanged or carries one atom of a set of identical atoms into a position of another atom of the set, the result will be indistinguishable from the existing initially;

(iii) when this is the result of the symmetry operation, the molecule does indeed have the corresponding symmetry elements and

(iv) The symmetry elements that any molecule can possess are E, C_n, σ, I, and S_n.

6.0 Tutor marked assignment

(a) determine the point groups of the following objects. (a) A sphere (b) A rectangular sheet of paper (c) A cone

(b) briefly explain the effect symmetry on the properties of molecules.

7.0 Further reading and other resources

Atkins, P. W. (1982). Physical Chemistry, (2_{nd} ed.), Oxford, Oxford University Press.

Babarinde, A. (2008). Introduction to Symmetry and Group Theory, (1_{st} ed.), Ijebu-Ode, Luck Odoni.

Barrow, G. M. (1982). Physical Chemistry (4_{th} ed.), Auckland, McGraw-Hill.

Newcastle (2009) Retrieved August 6, 2009 from website: www.phys.ncl.ac.uk