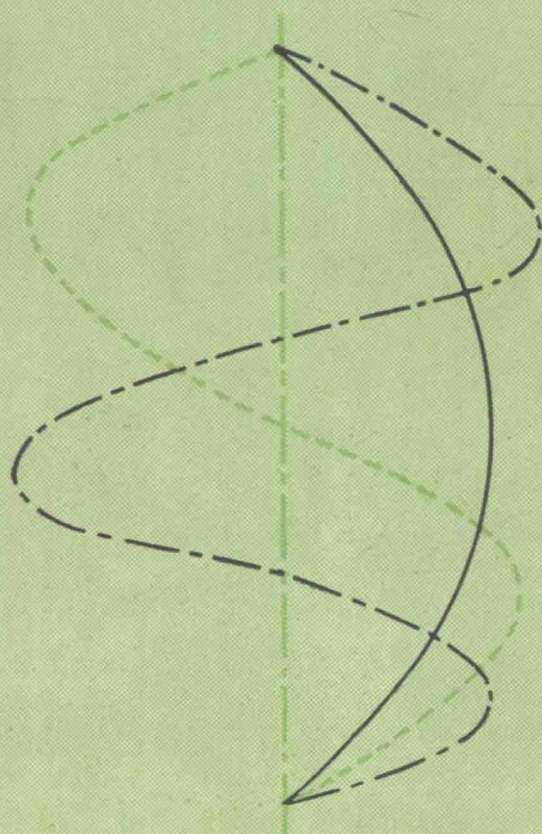


# INTRODUCTORY QUANTUM CHEMISTRY

SECOND EDITION



A.K. CHANDRA

# Introductory QUANTUM CHEMISTRY

SECOND EDITION

**A. K. CHANDRA**

Indian Institute of Science  
Bangalore



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## ***Preface to the Second Edition***

It is gratifying to note that most chapters in this book have received endorsement by a considerable number of students and teachers of various universities in India. I am grateful to all who have written to me, some drawing attention to minor errors and others suggesting addition of a few more chapters on certain special topics. Most of them strongly recommended including a chapter on "Symmetry". This new edition has, therefore, a chapter on the principles of symmetry and their applications in chemistry. Besides, a few additions, such as the simple Huckel treatment of the cyclic conjugated systems and aromaticity have been incorporated in Chapter 8. For the new chapter a set of problems are given and worked out in detail in the "Answers to the Problems" section. These problems are so chosen as to supplement the knowledge already acquired by the reader from the text.

I would like to thank my colleagues Dr D N Sathyanarayana and Prof. K. Venkatesan for their careful reading of the new chapter (Chapter 9) and making several critical suggestions. Finally, I would like to record my appreciation of the assistance of Mr S Srirama who typed the manuscript and Mr Venugopal for preparing the diagrams.

A. K. CHANDRA

# Preface to the First Edition

When I started writing this manuscript, I did not have the honest intention of ever completing this for a university level textbook on quantum chemistry. Thanks are due to the University Grants Commission (Government of India) not only for providing me with enough funds for the preparation of the manuscript but also for their asking me to submit progress reports every six months. I found a great difficulty in writing a progress report for them without making any real progress in this work.

The basic material of this book is based on my lectures to the post-graduate students in the Department of Pure Chemistry, Calcutta University, for several years, in the Department of Chemistry, Indian Institute of Technology, Bombay, for a year or so, and at present in the Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore. This book is therefore primarily intended for students of chemistry at the M.Sc. level in India, and possibly at the senior undergraduate levels in the British and American universities. Teachers and research workers who are not actively engaged in this particular field of chemistry but wish to keep up with the recent trends in chemical education will find this book very useful. This book contains chapters that are basic to an understanding of the important concepts that quantum mechanics has introduced in chemistry. Since an adequate and critical comprehension can only be achieved if they are presented in mathematical language, considerable efforts have been made to make the mathematics simple and comprehensive. However, I have assumed that a typical reader has been exposed at sometime to an introductory course in physics, calculus, vectors and determinant.

This book covers the most recent advances in this field in various chapters, especially in the last two chapters which explain the Woodward-Hoffmann rule and describe the chemical applications of the Hellmann-Feynman theory. These are important and significant topics, and at the same time simple enough for a typical reader to follow.

Every chapter, except the last one, is followed by a set of problems most of which are worked out in detail in the 'Answers to the Problems' section. These problems are chosen so as to supplement the knowledge already acquired by the reader from the text.

My sincere thanks are due to Dr. N. G. Mukherjee, Calcutta University, and Dr. B. M. Deh, Indian Institute of Technology, Bombay. Dr. Mukherjee read the entire manuscript in depth, made many suggestions for improvement and suggested many problems for several chapters

of this book, while Dr. Deb was the main author of the chapter on the Hellmann-Feynman theorem and some of its chemical applications. I would like to thank Dr. C. D. Flint, Birkbeck College, London University, for his careful reading of the chapters 5, 6 and 7 and making several critical suggestions when he was here as a visiting scientist. Thanks are due to Professor P. T. Narasimhan, Indian Institute of Technology, Kanpur, for his critical reading of the Chapters 3 and 4 and pointing out many obscurities in the previous version of these two chapters. Although various scholars, including my own students (Dr. D. C. Mukherjee of Calcutta University, and Mr. R. Sundar and Mr. B. S. Sudhindra, both of the Indian Institute of Science, Bangalore) have gone through some portions of this book, it is too much to hope that this book is free from any errors and obscurities. But the responsibility for these is entirely mine, and I shall be grateful to be told of the places where I could do better.

I could not end this Preface without an acknowledgement to the several lecture courses which I followed during my stay at Oxford, especially those of late Prof. C. A. Coulson, F.R.S., whose ideas and derivations may be found in several pages of this book. However, I feel, my greatest debt goes to my teacher, Prof. Sadhan Basu, Palit Professor of Chemistry, Calcutta University, whose lectures on various topics of quantum chemistry on various occasions at the University College of Science, Calcutta, when I was one of his pupils, created in me an immense interest in this field. Prof. A. B. Biswas, Indian Institute of Technology, Bombay, had the great kindness to advise me with many helpful suggestions concerning the plan and emphasis of this book. I would also like to thank Prof. Satish Dhawan, Director, and Prof. A. R. Vasudeva Murthy, Chairman of the Division of Chemical and Biological Sciences, Indian Institute of Science, for their positive encouragement and general help in this endeavour.

Finally, I would like to record my appreciation of the assistance of Mr. C. R. Sreenivasa Murthy who carefully typed and retyped the entire manuscript, and of my wife, Bani, for reading the proofs.

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### Energy Conversion Table

	a.u.	eV	cm <sup>-1</sup>	Kcal/mole	erg
1 a.u.	1	27.2	$2.1947 \times 10^5$	$6.277 \times 10^4$	$4.358 \times 10^{-11}$
1 eV	0.0367	1	$8.066 \times 10^3$	23.07	$1.602 \times 10^{-12}$
1 cm <sup>-1</sup>	$4.556 \times 10^{-6}$	$1.2398 \times 10^{-4}$	1	$2.86 \times 10^{-8}$	$1.9862 \times 10^{-16}$
1 Kcal/mole	$1.593 \times 10^{-8}$	0.0433	$3.4964 \times 10^3$	1	$6.9446 \times 10^{-14}$
1 erg molecule <sup>-1</sup>	$2.294 \times 10^{10}$	$6.24 \times 10^{11}$	$5.035 \times 10^{15}$	$1.44 \times 10^{13}$	1

### Fundamental Constants

Charge on electron	$e = 4.8 \times 10^{-10}$ esu
Velocity of light	$c = 2.998 \times 10^{10}$ cm/sec
Planck's constant	$h = 6.624 \times 10^{-27}$ erg sec.
Mass of electron	$m_e = 9.107 \times 10^{-28}$ gm
Mass of proton	$m_p = 1.673 \times 10^{-24}$ gm
Boltzmann constant	$k = 1.4 \times 10^{-16}$ erg degree <sup>-1</sup>
Rydberg constant	$R = 109737$ cm <sup>-1</sup> (for infinite nuclear mass)
Bohr radius	$a_0 = 0.529 \times 10^{-8}$ cm
Bohr magneton	$\beta = 0.927 \times 10^{-20}$ erg gauss <sup>-1</sup>

### Conversion Table in SI Units

Physical quantity	Old unit	Value in SI units
Distance	Centimetre	Metre, m 1 cm = $10^{-2}$ metre
Energy	Calorie (thermo-chemical)	4.184 J (joule)
	Electron volt—eV	$1.602 \times 10^{-19}$ J
	Erg	$10^{-7}$ J
	Wave number, cm <sup>-1</sup>	$1.986 \times 10^{-23}$ J
Force	Dyne	$10^{-5}$ N (Newton)
Pressure	Atmosphere	$1.013 \times 10^5$ Pa (Pascal)
	torr = mm Hg	133.3 Pa
Frequency	Cycle per second	1 Hz (hertz)
Relative permittivity	Dielectric constant	1
Temperature	°C and °K	1K (kelvin) 0°C = 273.2K
Mass	Gram	$10^{-3}$ kg (kilogram)
Charge of an electron	$4.8 \times 10^{-10}$ esu	$1.6021 \times 10^{-19}$ C
Dipole moment	Debye-D	$3.334 \times 10^{-30}$ C.m.

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# Introduction: Waves and Quanta

## 1.1. Wave and Particle Nature of Radiation

Radiation is known to be composed of electromagnetic waves with electric and magnetic fields perpendicular to each other and perpendicular to the direction of propagation. By definition, wavelength  $\lambda$  is the distance between the successive crests and the phase velocity  $\omega$  is the velocity at which a given crest moves (Fig. 1.1).

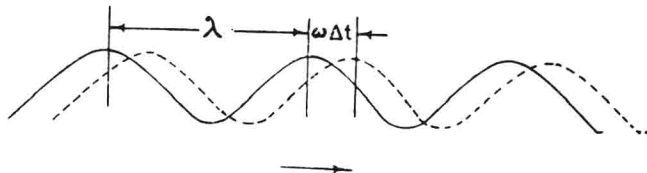


FIG. 1.1. *Electromagnetic wave at time  $t$  and  $t + \Delta t$ .*

There are quite a number of optical phenomena, notably the diffraction and the interference of radiation, which provide the strong evidence in favour of the wave nature of radiations.

There are, however, two other phenomena which provide equally strong evidence in favour of the particle nature of radiation. They are the photoelectric effect and the Compton scattering. In the photoelectric effect electrons are emitted from a metal surface illuminated by the ultraviolet radiation. If the kinetic energy (KE) of the emitted electrons is plotted against the frequency  $\nu$  ( $= c/\lambda$ , where  $c$  is the velocity of light) of the incident radiation, a graph of the type shown in Fig. 1.2 is obtained. It has been observed that increasing the intensity of the incident radiation at constant frequency does not affect the KE of the emitted electrons but increases the number of electrons emitted in unit time. The equation of the straight line shown in Fig. 1.2 is

$$\text{KE} = h(\nu - \nu_0) \quad (1.1)$$

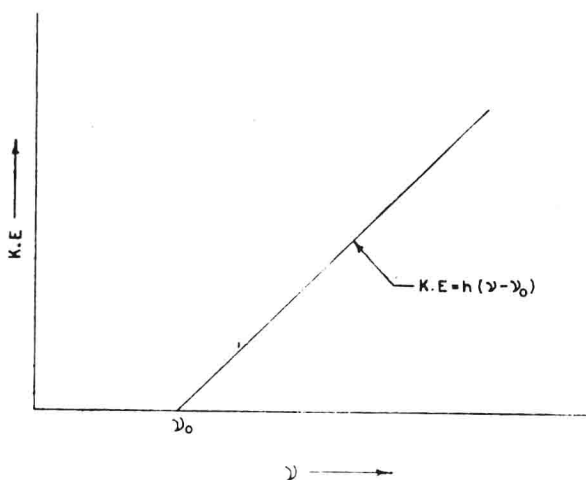


FIG. 1.2. Kinetic energy of photoelectrons.

where  $\nu_0$  is the minimum frequency below which no electron is emitted and  $h$  is called the Planck constant. This photoelectric phenomenon was explained by Einstein using Planck's quantum hypothesis that the energy of radiation is not distributed through waves, as the classical concept leads to, but is concentrated into corpuscles or photons of energy  $h\nu$ . It is further assumed that the emission of an electron from the metal surface takes place only when the electron receives a certain minimum energy, say  $h\nu_0$ , equivalent to the energy with which the electron is bound to the surface. Therefore, the KE of the emitted electrons is  $h(\nu - \nu_0)$ .

Since the energy  $E$  of a photon, according to Planck, is given by

$$E = h\nu \quad (1.2)$$

and the mass,  $m$  of the photon can be calculated using Einstein's relativistic equation

$$E = mc^2 \quad (1.3)$$

where  $c$  is the velocity of light, the momentum  $p$  of a photon is given by

$$p = mc \quad (1.4)$$

This momentum equation was tested by Compton in an experiment where photons were observed to be scattered at all angles by electrons of the scattering material. So, the electromagnetic radiation has both the particle and wave aspects. If the radiation can be treated as waves as well as particles then how do the real particles behave? One should expect that the behaviour of real particles must be capable of description in terms of waves. In 1924, de Broglie combined the ideas of Planck (Eq. 1.2) and Einstein (Eq. 1.3) into a relationship between mass and frequency.

$$mc^2 = h\nu \quad (1.5)$$

Hence, the relationship between velocity  $v$ , and momentum  $p$ , becomes

$$p = mv = \frac{h\nu}{c} = \frac{h}{\lambda} \quad (1.6)$$

Thus, it was possible to associate waves with every moving particle in nature. This relation should hold also for heavier particles which we are able to see. But, on account of heavier mass,  $\lambda$  becomes so small that there is a great difficulty in discovering the wave phenomenon associated with heavier particles. This concept of the wave-particle duality of matter was subjected to experimental test by Davisson and Germer in 1927 and independently by Thompson in 1928 who showed that a beam of electrons did indeed behave as if it were waves and underwent diffraction from a suitable grating.

## 1.2. Wave Equation

If electrons have the wave properties then there must be a wave equation and a wave function to describe the electron waves just as the waves of light, sound and strings are described. Let us consider the motion of a string which is held fixed at two ends  $x = 0$  and  $x = a$ . It is possible to excite with care certain kinds of vibrations in which all points of the string move so that their displacements vary with time in the same way and all points are at their maximum displacements at the same time and have their maximum velocity at the same time. If the displacement occurs in the  $y$ -direction, mathematically these motions can be described by functions of the form

$$y(x, t) = f(x) \phi(t) \quad (1.7)$$

where  $f(x)$  is independent of  $t$  and  $\phi(t)$  is independent of  $x$ . Such motions are called normal modes of vibration. The wave equation has the general form

$$\frac{d^2y}{dx^2} = \frac{1}{c^2} \frac{d^2y}{dt^2} \quad (1.8)$$

where  $c$  is called the wave velocity. Substituting for  $y$  from Eq. (1.7) in Eq. (1.8) one obtains

$$\frac{c^2}{f(x)} \frac{d^2f(x)}{dx^2} = \frac{1}{\phi(t)} \frac{d^2\phi(t)}{dt^2} = -\omega^2 \quad (1.9)$$

In Eq. (1.9) the variables are separated and they may be equated to the same constant, say  $-\omega^2$ . This gives us two ordinary differential equations

$$\frac{d^2\phi(t)}{dt^2} + \omega^2\phi(t) = 0 \quad (1.10)$$

$$\frac{d^2f(x)}{dx^2} + \frac{\omega^2 f(x)}{c^2} = 0 \quad (1.11)$$

(For solutions of the second order differential equations of this form, see Appendix 1).

Eq. (1.10) has the solution

$$\phi(t) = A \sin \omega t + B \cos \omega t \quad (1.12)$$

where the two constants  $A$  and  $B$  are determined from the boundary conditions, and  $\omega$  is called the circular frequency which is related to the ordinary frequency  $\nu$  as

$$\omega = 2\pi\nu \quad (1.13)$$

Eq. (1.11) may therefore be written as

$$\frac{d^2 f(x)}{dx^2} + \frac{4\pi^2 \nu^2}{c^2} f(x) = 0 \quad (1.14)$$

Setting  $\lambda = \frac{c}{\nu}$ , the general solution of Eq. (1.14) may be written as

$$f(x) = A_1 \exp\left(+\frac{i 2\pi x}{\lambda}\right) + A_2 \exp\left(-\frac{i 2\pi x}{\lambda}\right) \quad (1.15)$$

or as (see Appendix 1)

$$f(x) = C \sin \frac{2\pi}{\lambda} x + D \cos \frac{2\pi}{\lambda} x \quad (1.16)$$

where  $A_1$ ,  $A_2$ ,  $C$ , and  $D$  are constants. Let us consider Eq. (1.16) and impose the boundary conditions

(i)  $f(x) = 0$  at  $x = 0$ ; and

(ii)  $f(x) = 0$  at  $x = a$

where  $a$  is the length of the string. From the boundary condition (i),  $D = 0$  and from the condition (ii),

$$C \sin \frac{2\pi}{\lambda} a = 0$$

or 
$$\sin \frac{2\pi a}{\lambda} = 0$$

or 
$$\frac{2a}{\lambda} = n, \quad n = 1, 2, 3, \dots \quad (1.17)$$

where  $n$  is a positive integer. Thus

$$a = n \frac{\lambda}{2} \quad (1.18)$$

The normal modes are thus the stationary sine waves given by

$$f(x) = C \sin \frac{n\pi}{a} x \quad (1.19)$$

and the wavelengths  $\lambda$  are such that the length of the string is an integral number of half waves. The complete solution for a normal mode in a

stretched string therefore follows from Eqs. (1.17), (1.12), (1.13) and (1.19), and is given by

$$y(x, t) = C \sin \frac{n\pi}{a} x. (A \sin 2\pi\nu t + B \cos 2\pi\nu t) \quad \checkmark \quad (1.20)$$

Eq. (1.20) is an expression for the amplitude of waves generated during the normal modes of vibration in a stretched string. The same equation should represent the amplitude of a de Broglie wave associated with a moving particle. We are, primarily concerned here, with the time-independent or stationary waves. Therefore, the equation for a standing sine wave of wavelength  $\lambda$  is given by

$$\psi = C \sin \frac{2\pi}{\lambda} x \quad (1.21)$$

where  $\psi$ , called the wave function, is the amplitude of the wave varying sinusoidally along  $x$  and  $C$  is the maximum amplitude. Double differentiation of Eq. (1.21) with respect to  $x$  gives

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} C \sin \frac{2\pi}{\lambda} x = -\frac{4\pi^2}{\lambda^2} \psi \quad (1.22)$$

The kinetic energy  $T$  of a moving particle of mass  $m$  and velocity  $v$  is given by

$$T = \frac{1}{2} mv^2 = \frac{m^2 v^2}{2m} \quad (1.23)$$

Following the de Broglie relation [Eq. (1.6)],  $T$  becomes

$$T = \frac{h^2}{2m\lambda^2} \quad (1.24)$$

By using Eq. (1.22) to eliminate  $\lambda^2$  from Eq. (1.24) we get

$$T = -\frac{h^2}{8\pi^2 m} \cdot \frac{1}{\psi} \frac{d^2\psi}{dx^2} \quad (1.25)$$

If the particle moves in a field whose potential energy is  $V$ , then

$$T = E - V = -\frac{h^2}{8\pi^2 m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} \quad (1.26)$$

where  $E$  is the total energy. This is Schrodinger's equation for a particle in one dimension. It is usually written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad (1.27)$$

In three dimensions this equation becomes:

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad (1.28)$$

### 1.3. The Interpretation of $\psi$

In classical mechanics the square of wave amplitude associated with electromagnetic radiation is interpreted as a measure of the radiation

intensity. This suggests that we should make a similar association for de Broglie waves associated with electrons or any particle. Let the solution of wave equation (1.28) be a function  $\psi(x, y, z)$ , called wave function. We may anticipate that some physically observable property of the electron is connected to  $\psi^2(x, y, z)$  or more generally  $\psi^*(x, y, z)\psi(x, y, z)$  if  $\psi$  is a complex wave function.<sup>1</sup> For a system having electrons there are two ways in which  $\psi^2$  or  $\psi^*\psi$  can be interpreted. Either  $|\psi^2|$  may be regarded as a measure of the density of electrons or  $|\psi^2| d\tau$  be interpreted as a measure of probability of finding the electron in a small volume  $d\tau$  in a certain region of space.

The latter view is consistent with the Heisenberg uncertainty principle based on results of some experiments. This principle states that the position and momentum of a small particle like electron cannot simultaneously be measured exactly; for in measuring the position of an electron we have to disturb it and so change its momentum. A complete analysis shows that if  $\Delta x$  and  $\Delta p_x$  are the uncertainties in position and momentum then  $\Delta x \Delta p_x \sim h$ . Under such circumstances the best thing one can do is to predict the probability that an electron is found in a given region of space. For this reason  $|\psi^2|$  may be called the probability function. Since electron must be somewhere in space, the integration of  $|\psi^2|$  over all space must be unity, so that

$$\int |\psi^2| d\tau = 1 \quad (1.29)$$

Such wave functions are said to be normalised. For every system which is bound, every wave function must satisfy Eq. (1.29).

#### 1.4. Properties of $\psi$

A second-order differential equation like (1.28) may give rise to several solutions though not necessarily all of them correspond to any physical or chemical reality. Such wave functions are therefore considered unacceptable. Acceptable wave functions are those which satisfy the following conditions:

1.  $\psi$  is single valued, i.e. for each value of the variables  $x, y, z$ , there is only one value of the function  $\psi$ . If one of the variables is an angle, say  $\theta$ , then it requires that

$$\psi(\theta) = \psi(\theta + 2n\pi)$$

where  $n$  is an integer.

2.  $\psi$  and its first derivative with respect to its variables are continuous. In other words, there must not exist any sudden changes in  $\psi$  as its variables are changed.
3. For bound states  $\psi$  must vanish at infinity. If  $\psi$  be a complex function, then  $\psi^*\psi$  must vanish at infinity.

<sup>1</sup> If  $\psi = a + ib$  where  $i = \sqrt{-1}$ , then  $\psi^* = a - ib$ , so that  $\psi^*\psi = a^2 + b^2$ , a real function.

If the above three conditions are satisfied the function  $\psi$  is called a well-behaved function.

## APPENDIX 1

In this appendix we will show how a simple differential equation of the second order of the following form

$$\frac{d^2y}{dx^2} + k^2y = 0 \quad (\text{A1.1})$$

can be solved. In Eq. (A1.1)  $k^2$  is constant. Such an equation is satisfied by a function of an exponential form. Let us assume the solution of Eq. (A1.1) as

$$y = \exp(mx) \quad (\text{A1.2})$$

Then substituting for  $y$ ,  $\exp(mx)$  in Eq. (A1.1), we obtain the auxiliary equation

$$m^2 + k^2 = 0 \quad (\text{A1.3})$$

The roots of Eq. (A1.3) are given by

$$m = \pm ik \quad (\text{A1.4})$$

where  $i = \sqrt{-1}$ . The particular solutions of Eq. (A1.1) are  $\exp(+ikx)$  and  $\exp(-ikx)$ . On adding these particular solutions there results a solution with two independent arbitrary constants and therefore the complete solution of Eq. (A1.1) is written as

$$y = A_1 \exp(ikx) + A_2 \exp(-ikx) \quad (\text{A1.5})$$

On expanding the exponentials in sines and cosines we obtain the following equivalent form

$$\begin{aligned} y &= A_1 (\cos kx + i \sin kx) + A_2 (\cos kx - i \sin kx) \\ &= (A_1 + A_2) \cos kx + (A_1 - A_2) i \sin kx \\ &= C \cos kx + D \sin kx \end{aligned} \quad (\text{A1.6})$$

In Eqs. (A1.5) and (A1.6),  $A_1$ ,  $A_2$ ,  $C$ , and  $D$  are arbitrary constants.

## PROBLEMS

1. An electron moves in an electric field with kinetic energy of 2.5 eV. What is its associated de Broglie wavelength?
2. Find the energy jump in electron volts for the emission of visible light of wavelength 7500 Å.
3. Show that as  $x$  increases by  $\lambda$  in the wave

$$\psi = A \exp\left(\frac{2\pi ix}{\lambda}\right)$$

the amplitude,  $\psi$  goes through one cycle.



# 2

## Operator Concept in Quantum Chemistry

### 2.1. Operators

We have learnt in the previous chapter that wave function describes the state of a system so that any observable quantity can be derived from it. The mathematical process for carrying out the derivation involves the concept of operators. *To every physically measurable or observable quantity like position, velocity, linear momentum, angular momentum, energy, etc. of a system there corresponds an operator in quantum mechanics.* This may be treated as one of the several basic postulates of quantum mechanics.

An operator is a symbol for a certain mathematical procedure which transforms one function into another. For example, the operator of evaluating the derivative with respect to  $x$  is represented by the symbol  $d/dx$ . When this operator is applied to the function  $x^n$  we obtain a new function as

$$\frac{d}{dx}(x^n) = nx^{n-1}$$

A list of typical examples of different mathematical operations along with the results of the operations on the function,  $x^3$  is given in Table 1.

TABLE 1

Operation	Operator	Result of operation on $x^3$
Taking the square	$(\quad)^2$	$x^6$
Taking the square root	$\sqrt{\quad}$	$x^{3/2}$
Multiplication by a constant $k$	$k$	$kx^3$
Differentiation with respect to $x$	$\frac{d}{dx}$	$3x^2$
Integration with respect to $x$	$\int (\quad) dx$	$x^4/4 + c$

Evidently, an operator is a set of instructions embodied in the definition of the operator and the operations can always be written in the form of an equation