

# Preface

Computational chemistry and molecular modeling is a fast emerging area which is used for the modeling and simulation of small chemical and biological systems in order to understand and predict their behavior at the molecular level. It has a wide range of applications in various disciplines of engineering sciences, such as materials science, chemical engineering, biomedical engineering, etc. Knowledge of computational chemistry is essential to understand the behavior of nanosystems; it is probably the easiest route or gateway to the fast-growing discipline of nanosciences and nanotechnology, which covers many areas of research dealing with objects that are measured in nanometers and which is expected to revolutionize the industrial sector in the coming decades.

Considering the importance of this discipline, computational chemistry is being taught presently as a course at the postgraduate and research level in many universities. This book is the result of the need for a comprehensive textbook on the subject, which was felt by the authors while teaching the course. It covers all the aspects of computational chemistry required for a course, with sufficient illustrations, numerical examples, applications, and exercises. For a computational chemist, scientist, or researcher, this book will be highly useful in understanding and mastering the art of chemical computation. Familiarization with common and commercial software in molecular modeling is also incorporated. Moreover, the application of the concepts in related fields such as biomedical engineering, computational drug designing, etc. has been added.

The book begins with an introductory chapter on computational chemistry and molecular modeling. In this chapter (Chap. 1), we emphasize the four computational criteria for modeling any system, namely stability, symmetry, quantization, and homogeneity. In Chap. 2, “Symmetry and Point Groups”, elements of molecular symmetry and point group are explained. A number of illustrative examples and diagrams are given. The transformation matrix for each symmetry operation is included to provide a computational know-how. In Chap. 3, the basic principles of quantum mechanics are presented to enhance the reader’s ability to understand the quantum mechanical modeling techniques. In Chaps. 4–10, computational techniques with different levels of accuracy have been arranged. The chapters also

cover Huckel's molecular orbital theory, Hartree-Fock (HF) approximation, semi-empirical methods, ab initio techniques, density functional theory, reduced density matrix, and molecular mechanics methods.

Topics such as the overlap integral, the Coulomb integral and the resonance integral, the secular matrix, and the solution to the secular matrix have been included in Chap. 4 with specific applications such as aromaticity, charge density calculation, the stability and delocalization energy spectrum, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), bond order, the free valence index, the electrophilic and nucleophilic substitution, etc. In the chapter on HF theory (Chap. 5), the formulation of the Fock matrix has been included. Chapter 6 concerns different types of basis sets. This chapter covers in detail all important minimal basis sets and extended basis sets such as GTOs, STOs, double-zeta, triple-zeta, quadruple-zeta, split-valence, polarized, and diffuse. In Chap. 7, semi-empirical methods are introduced; besides giving an overview of the theory and equations, a performance of the methods based on the neglect of differential overlap, with an emphasis on AM1, MNDO, and PM3 is explained. Chapter 8 is on ab initio methods, covering areas such as the correlation technique, the Möller-Plesset perturbation theory, the generalized valence bond (GVB) method, the multi-configurations self consistent field (MCSCF) theory, configuration interaction (CI) and coupled cluster theory (CC).

Density functional theory (DFT) seems to be an extremely successful approach for the description of the ground state properties of metals, semiconductors, and insulators. The success of DFT not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes. The chapter on density functional theory (Chap. 9) covers the entire applications of the theory.

Chapter 10 explains reduced density matrix and its applications in molecular modeling. While traditional methods for computing the orbitals are scaling cubically with respect to the number of electrons, the computation of the density matrix offers the opportunity to achieve linear complexity. We describe several iteration schemes for the computation of the density matrix. We also briefly present the concept of the best  $n$ -term approximation.

Chapter 11 is on molecular mechanics and modeling, in which various force fields required to express the total energy term are introduced. Computations using common molecular mechanics force fields are explained.

Computations of molecular properties using the common computational techniques are explained in Chap. 12. In this chapter, we have included a section on a comparison of various modeling techniques. This helps the reader to choose the method for a particular computation.

The need and the possibility for high performance computing (HPC) in molecular modeling is explained in Chap. 13. This chapter explains HPC as a technique for providing the foundation to meet the data and computing demands of Research and Development (R&D) grids. HPC helps in harnessing data and computer resources in a multi-site, multi-organizational context effective cluster management, making use of maximum computing investment for molecular modeling.

Some typical projects/research topics on molecular modeling are included in Chap. 14. This chapter helps the reader to familiarize himself with the modern trends in research connected with computational chemistry and molecular modeling.

Chapter 15 is on basic mathematics and contains an introduction to computational tools such as Microsoft Excel, MATLAB, etc. This helps even a non-mathematics person to understand the mathematics used in the text to appreciate the real art of computing. Sufficient additions have been included as an appendix to cover areas such as operators, HuckelMO hetero atom parameters, Microsoft Excel in the balancing of chemical equations, simultaneous spectroscopic analysis, the computation of bond enthalpy of hydrocarbons, graphing chemical analysis data, titration data plotting, the application of curve fitting in chemistry, the determination of solvation energy, and the determination of partial molar volume.

An exclusive URL (<http://www.amrita.edu/cen/ccmm>) for this book with the required support materials has been provided for readers which contains a chapterwise PowerPoint presentation, numerical solutions to exercises, the input/output files of computations done with software such as Gaussian, Spartan etc., HTML-based programming environments for the determination of eigenvalues/eigenvectors of symmetrical matrices and interconversion of units, and the step-by-step implementation of cluster computing. A comprehensive survey covering the possible journals, publications, software, and Internet support concerned with this discipline have been included.

The uniqueness of this book can be summarized as follows:

1. It provides a comprehensive background theory for molecular modeling.
2. It includes applications from all related areas.
3. It includes sufficient numerical examples and exercises.
4. Numerous explanatory illustrations/figures are included.
5. A separate chapter on basic mathematics and application tools such as MATLAB is included.
6. A chapter on high performance computing is included with examples from molecular modeling.
7. A chapter on chemical computation using the reduced density matrix method is included.
8. Sample projects and research topics from the area are included.
9. It includes an exclusive web site with required support materials.

With the vast teaching expertise of the authors, the arrangement and designing of the topics in the book has been made according to the requirements/interests of the teaching/learning community. We hope that the reader community appreciates this. Computational chemistry principles extended to molecular simulation are not included in this book; we hope that a sister publication of this book covering that aspect will be released in the near future. We have tried to make the explanations clear and complete to the satisfaction of the reader. However, regarding any queries, suggestions, corrections, modifications and advice, the readers are always welcome to contact the authors at the following email address: [n\\_krishnan@ettimadai.amrita.edu](mailto:n_krishnan@ettimadai.amrita.edu).

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## Chapter 3

# Quantum Mechanics: A Brief Introduction

*I think it is safe to say that no one understands quantum mechanics. Do not keep saying to yourself, if you can possibly avoid it, "But how can it be like that?" because you will get "down the drain" into a blind alley from which nobody has yet escaped. Nobody knows how it can be like that.*

– Richard Feynman (1918–1988)

### 3.1 Introduction

The development of quantum mechanics was initially provoked by two main observations that established the inadequacy of classical physics. They are called the *ultraviolet catastrophe* and the *photoelectric effect*.

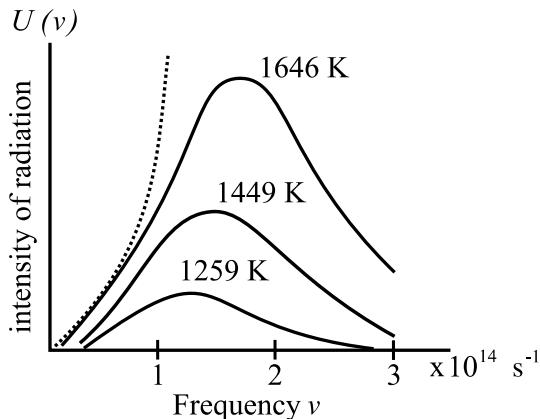
#### 3.1.1 The Ultraviolet Catastrophe

A blackbody is a unique object which absorbs and emits all frequencies of electromagnetic radiations incident on it. Classical physics can be used to derive an equation which describes the intensity of blackbody radiation as a function of frequency for different temperatures. This generalization is known as the Rayleigh-Jeans law. Let us look at the spectrum in detail. When an iron block is heated, the color of the metal is gray at a low temperature, bright red at about 1270 K and dazzling white at 1770 K. This feature is described in Fig. 3.1. Although the Rayleigh-Jeans law works for low frequencies, it diverges at higher ones. This divergence at higher frequencies is called the ultraviolet catastrophe.

Max Planck [1] gave an explanation to the blackbody spectrum in the year 1900 by assuming that the energies of the oscillations of electrons which gave rise to the radiation must be proportional to integral multiples of the frequencies. Using statistical mechanics, Planck derived an equation similar to the Rayleigh-Jeans equation, but with the adjustable parameter  $h$ . Planck found that for  $h = 6.626 \times 10^{-34}$  J s (Planck's constant), the experimental data could be reproduced to its finest detail. This famous revolutionary relation is given by Eq. 3.1.

$$E = nh\nu \quad (3.1)$$

**Fig. 3.1** Intensity of radiation of heated iron against frequency. The values corresponding to the Rayleigh-Jeans relationship are represented by a *dashed curve*. It fits well to experimental data at low frequencies, but becomes departing at higher frequencies



Where  $n$  is a positive integer,  $\vartheta$  is the frequency of the oscillator, and  $E$  is the energy. But Planck could not offer a good justification for his assumption of energy quantization. Scientists did not take this energy quantization idea seriously until Einstein invoked a similar assumption to explain the photoelectric effect.

### 3.1.2 The Photoelectric Effect

Heinrich Hertz in 1887 discovered that irradiation by ultraviolet light would cause electrons to be ejected from a metal surface. According to the classical wave theory of light, the intensity of the light determines the amplitude of the wave, and so a greater intensity of light should cause the electrons on the metal to oscillate more violently and to be ejected with a greater kinetic energy. In contrast, the experiment showed that the kinetic energy of the ejected electrons depended only on the frequency of the light. On the other hand, the intensity of light affects only the number of ejected electrons and not their kinetic energies.

Einstein explained the problem of the photoelectric effect in 1905. Instead of assuming that the electronic oscillators had energies given by Planck's equation (Eq. 3.1), Einstein assumed that the radiation itself consisted of packets of energy  $E$ , which are now called photons. Einstein successfully explained the photoelectric effect by using this assumption, and he calculated a value of  $h$  close to that obtained by Planck.

Two years later, Einstein showed that, like light, atomic vibrations were also quantized. Classical physics predicts that the molar heat capacity at a constant volume ( $C_v$ ) of a crystal is  $3R$ , where  $R$  is the molar gas constant. This works well for high temperatures, but for low temperatures  $C_v$  actually falls to zero. Einstein was able to explain this result by assuming that the oscillations of atoms about their equilibrium positions are quantized according to Eq. 3.1 – Planck's quantization condi-

tion for electronic oscillators. This confirmed that the energy quantization concept was important even for a system of atoms in a crystal, which could be well-modeled by a system of masses and springs (i.e., by classical mechanics).

### 3.1.3 The Quantization of the Electronic Angular Momentum

Rutherford proposed a classical atomic structure in which the electrons are considered as revolving round the nucleus of atom. One problem with this model is that orbiting electrons experience a centripetal acceleration. Such accelerating charges should lose energy by radiation making stable electronic orbits classically forbidden. Bohr proposed stable electronic orbits with the electronic angular momentum quantized as:

$$l = mvr = n\hbar \quad (3.2)$$

where  $m$  is the mass of the electron,  $v$  its velocity, and  $r$  the radius of the orbit,  $\hbar = h/2\pi$ ,  $n = 1, 2, 3, \dots$ . The quantization of angular momentum leads to discretization of radius as well as the energy of the orbit. Bohr's atom model could explain the atomic spectrum of the hydrogen atom. Bohr assumed that the discrete lines seen in the spectrum of the hydrogen atom were due to transitions of electrons from one allowed orbit/energy level to another. He further assumed that the energy of a transition is acquired or released in the form of a photon as proposed by Einstein, such that:

$$\Delta E = h\vartheta \quad (3.3)$$

This is known as the *Bohr frequency condition*. This condition, along with Bohr's expression for the allowed energy levels, gives a good match to the observed hydrogen atom spectrum. However, it works only for atoms with one electron. It could not explain the fine spectrum even for the hydrogen atom.

### 3.1.4 Wave-Particle Duality

Einstein had shown that the momentum of a photon is:

$$p = \frac{h}{\lambda} \quad (3.4)$$

This can be easily shown as follows. Assuming  $E = h\nu$  for a photon and  $\lambda\nu = c$  for an electromagnetic wave, we obtain:

$$E = \frac{hc}{\lambda} \quad (3.5)$$

Now we use the result of Einstein's special theory of relativity,  $E = mc^2$  to get:

$$\lambda = \frac{h}{mc} \quad (3.6)$$

This is equivalent to Eq. 3.4. Here,  $m$  refers to the relativistic mass, not the rest mass. Note that the rest mass of a photon is zero. Light can behave both as a wave (it exhibits properties such as diffraction, interference, and polarization, and it has a wavelength), and as a particle (it contains packets of energy  $h\nu$ ). De Broglie established a similar relationship in 1924 for material particles by proposing a dual nature for matter, and particles as well as waves [2]. He proposed an equation for finding the wave length ( $\lambda$  – the de Broglie wave length) included in Eq. 3.7, which is similar to Eq. 3.6. Here,  $m$  is mass, and  $v$  is the velocity of the particle.

$$\lambda = \frac{h}{mv} \quad (3.7)$$

In 1927, Davisson and Germer observed diffraction patterns by bombarding metals with electrons, confirming de Broglie's proposition.

De Broglie's equation offers a justification for Bohr's assumption (Eq. 3.2). According to Bohr's atom model, only those circular orbits in which the angular momentum of the electron, an integral multiple of  $\hbar = \frac{h}{2\pi}$  is permitted.

$$mvr = n\hbar = n\frac{h}{2\pi} \quad (3.8)$$

According to de Broglie, the electrons have a wave character also. For the waves to be completely in phase, the circumference of the orbit should be an integral multiple of wavelength. Therefore:

$$2\pi r = n\lambda \quad (3.9)$$

Where,  $r$  is the radius of the orbit. Substituting  $\lambda$  from Eq. 3.7:

$$mvr = n\hbar = n\frac{h}{2\pi} \quad (3.10)$$

This is identical with Bohr's equation (Eq. 3.3).

Heisenberg showed that the wave-particle duality leads to the famous uncertainty principle:

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad (3.11)$$

where  $\Delta x$  is the uncertainty in position and  $\Delta p$  is the uncertainty in momentum. One result of the uncertainty principle is that if the orbital radius of an electron in an atom  $r$  is known exactly, then the angular momentum must be uncertain. The problem with Bohr's model is that it specifies  $r$  exactly and it also ensures that the orbital angular momentum must be an integral multiple of  $\hbar = \frac{h}{2\pi}$ . Thus, the stage was



set for a new quantum theory, which was consistent with the uncertainty principle. The first principle in quantum theory stands for Schrödinger equation. Modeling molecules from the first principle is generally referred to as *ab initio modeling* [3].

## 3.2 The Schrödinger Equation

In 1925, Erwin Schrödinger and Werner Heisenberg independently developed the new quantum theory. Schrödinger method involves partial differential equations, whereas Heisenberg's method employs matrices; however, a year later the two methods were shown to be mathematically equivalent. Schrödinger equation seems to have a better physical interpretation via the classical wave equation. Indeed, the Schrödinger equation can be viewed as a form of the wave equation applied to matter waves.

### 3.2.1 The Time-Independent Schrödinger Equation

We start with the one-dimensional classical wave equation:

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} \quad (3.12)$$

where  $v$  is velocity.

By introducing the separation of variables:

$$u(x, t) = \psi(x)f(t) \quad (3.13)$$

we obtain:

$$f(t) \frac{d^2 \psi(x)}{dx^2} = \frac{1}{v^2} \psi(x) \frac{d^2 f(t)}{dt^2} \quad (3.14)$$

If we introduce one of the standard wave equation solutions for  $f(t)$  such as  $e^{i\omega t}$  (the constant can be taken care of later in the normalization), we obtain:

$$\frac{d^2 \psi(x)}{dx^2} = \frac{-\omega^2}{v^2} \psi(x) \quad (3.15)$$

Now we have an ordinary differential equation describing the spatial amplitude of the matter wave as a function of position. The energy of a particle is the sum of

kinetic and potential parts:

$$E = \frac{p^2}{2m} + V(x) \quad (3.16)$$

which can be solved for the momentum,  $p$ , to obtain:

$$p = \{2m[E - V(x)]\}^{1/2} \quad (3.17)$$

Now we can use the de Broglie formula (Eq. 3.4) to get an expression for the wavelength:

$$\lambda = \frac{h}{p} = \frac{h}{\{2m[E - V(x)]\}^{1/2}} \quad (3.18)$$

The term  $\omega^2/v^2$  in Eq. 3.15 can be rewritten in terms of  $\lambda$  if we recall that  $\omega = 2\pi\vartheta$  and  $\vartheta\lambda = v$ , where  $\omega$  is the angular momentum,  $\lambda$  is the wavelength and  $\vartheta$  is the frequency:

$$\frac{\omega^2}{v^2} = \frac{4\pi^2\vartheta^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m[E - V(x)]}{\hbar^2} \quad (3.19)$$

(where  $\hbar = h/2\pi$ ). When this result is substituted into Eq. 3.15 we obtain the famous *time-independent Schrödinger equation* [4]:

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (3.20)$$

which is almost always written in the form:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (3.21)$$

This single-particle one-dimensional equation can easily be extended to the case of three dimensions, where it becomes:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) = E\psi(r) \quad (3.22)$$

A two-body problem can also be treated by this equation if the mass  $m$  is replaced with a reduced mass.

It is important to point out that this analogy with the classical wave equation only goes so far. We cannot, for instance, derive the *time-dependent* Schrödinger equation in an analogous fashion (for instance, that equation involves the partial first derivative with respect to time instead of the partial second derivative). In fact, Schrödinger (see Fig. 3.2) presented his time-independent equation first, and then went back and postulated the more general time-dependent equation.

**Fig. 3.2** Erwin Schrödinger  
(1887–1961)



*A careful analysis of the process of observation in atomic physics has shown that the sub-atomic particles have no meaning as isolated entities, but can only be understood as inter-connections between the preparation of an experiment and the subsequent measurement.*

– Erwin Schrödinger

### 3.2.2 The Time-Dependent Schrödinger Equation

We are now ready to consider the time-dependent Schrödinger equation. Although we were able to derive the single-particle time-independent Schrödinger equation starting from the classical wave equation and the de Broglie relation, the time-dependent Schrödinger equation cannot be derived using elementary methods and is generally given as a postulate of quantum mechanics. The single-particle three-dimensional time-dependent Schrödinger equation is:

$$i\hbar \frac{\partial \psi(r,t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(r,t) + V(r)\psi(r,t) \quad (3.23)$$

where  $V$  is assumed to be a real function and represents the potential energy of the system. *Wave mechanics* is the branch of quantum mechanics with Eq. 3.23 as its dynamical law. Note that Eq. 3.23 does not yet account for spin or relativistic effects.

Of course the time-dependent equation can be used to derive the time-independent equation. If we write the wavefunction as a product of spatial and temporal terms,  $\psi(r,t) = \psi(r)f(t)$ , then Eq. 3.23 becomes

$$\psi(r)i\hbar \frac{df(t)}{dt} = f(t) \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) \quad (3.24)$$

$$\text{Or : } \frac{i\hbar}{f(t)} \frac{df}{dt} = \frac{1}{\psi(r)} \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) \quad (3.25)$$

Since the left-hand side is a function of  $t$  only and the right hand side is a function of  $r$  only, the two sides must equal a constant. If we tentatively designate this

constant  $E$  (since the right-hand side clearly must have the dimensions of energy), then we extract two ordinary differential equations, namely:

$$\frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{iE}{\hbar} \quad (3.26)$$

and

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r) \right] = E\psi(r) \quad (3.27)$$

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) = E\psi(r) \quad (3.28)$$

where the term in square bracket on the LHS is called the Hamiltonian operator.

The latter equation is once again the time-independent Schrödinger equation. The former equation is easily solved to yield:

$$f(t) = e^{-iEt/\hbar} \quad (3.29)$$

The Hamiltonian in Eq. 3.27 is a Hermitian operator, and the eigenvalues of a Hermitian operator must be real, so  $E$  is real. This means that the solutions  $f(t)$  are purely oscillatory, since  $f(t)$  never changes in magnitude (recall Euler's formula  $e^{\pm i\theta} = \cos \theta \pm i \sin \theta$ )

Thus, if:

$$\psi(r,t) = \psi(r)e^{-iEt/\hbar} \quad (3.30)$$

then the total wavefunction  $\psi(r,t)$  differs from  $\psi(r)$  only by a phase factor of a constant magnitude. There are some interesting consequences of this. Firstly, the quantity  $\psi(r,t)^2$  is time independent, as we can easily show:

$$|\psi(r,t)|^2 = \psi^*(r,t)\psi(r,t) = e^{iEt/\hbar}\psi^*(r)e^{-iEt/\hbar}\psi(r) = \psi^*(r)\psi(r) \quad (3.31)$$

Secondly, the expectation value for any time-independent operator is also time-independent, if  $\psi(r,t)$  satisfies Eq. 3.30. By the same reasoning applied above,

$$\langle A \rangle = \int \psi^*(r,t)\hat{A}\psi(r,t) = \int \psi^*(r)\hat{A}\psi(r) \quad (3.32)$$

For these reasons, wavefunctions of the type in Eq. 3.30 are called *stationary states*. The state  $\psi(r,t)$  is qustationary, but the particle it describes is not!

Of course, Eq. 3.30 represents a particular solution to Eq. 3.23. The general solution to Eq. 3.23 will be a linear combination of these particular solutions, i.e.:

$$\psi(r,t) = \sum_i c_i e^{-iEt/\hbar} \psi_i(r) \quad (3.33)$$

### 3.3 The Solution to the Schrödinger Equation

Solutions to Schrödinger equation are called wavefunctions. Out of various solutions to the Schrödinger equation, those satisfying the following conditions are listed here: [5]

1.  $\psi$  must be continuous. The wavefunction and its derivative must be continuous.
2.  $\psi$  must be finite everywhere.
3. It must approach zero at infinite distance.
4.  $\psi$  must be single-valued.

Solutions that do not satisfy these properties do not generally correspond to physically realizable circumstances. These permitted solutions to the equation are called eigenfunctions. Each permitted solution corresponds to a definite energy state and is known as orbital. The electron orbitals in atoms are called atomic orbitals, while those in a molecule are called molecular orbitals.

A typical quantum mechanical problem consists of the following steps:

1. Writing the Schrödinger equation for the system under study.
2. Solving the equation and finding the eigenvalues corresponding to the equation.
3. Characterizing the system based on the solutions.

Please refer to the Appendix to learn more about operators.

### 3.4 Exercises

#### 3.4.1 Question 1

What should be the range values of the work function of a metal in order to be useful in a photo cell for detecting visible light?

#### 3.4.2 Answer 1

A wave length ( $\lambda$ ) of visible light is 4000–7000 Å. Here:

$$h = 6.626 \times 10^{-34} \text{ J s}$$

$$c = 3 \times 10^8 \text{ m s}^{-1}$$

$$\text{and } 1 \text{ Joule} = \frac{1}{1.602 \times 10^{-19}} \text{ eV}$$

Energy corresponding to 4000 Å:

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10} \times 1.602 \times 10^{-19}} = 3.102 \text{ eV}$$

Similarly energy corresponding to 7000 Å

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{7000 \times 10^{-10} \times 1.602 \times 10^{-19}} = 1.77 \text{ eV}$$

Therefore, any metal with work function between 1.77 eV and 3.10 eV are the probable candidates for detecting visible light.

### 3.4.3 Question 2

Calculate the potential difference that must be applied to stop the fastest photo electrons emitted by a surface when irradiated by an electromagnetic radiation of frequency  $1.5 \times 10^{15}$  Hz. (The work function is 4 eV.)

### 3.4.4 Answer 2

$$\begin{aligned} \text{Energy of photon} = h\nu &= (6.626 \times 10^{-34}) \times (1.5 \times 10^{15}) \text{ J} \\ &= \frac{(6.626 \times 10^{-34}) \times (1.5 \times 10^{15})}{(1.602 \times 10^{-19})} \text{ eV} = 6.204 \text{ eV} \end{aligned}$$

Therefore, the energy for the fastest photo electron is  $6.204 - 4 = 2.204$  eV. Or, the potential difference to be applied is 2.204 volts.

### 3.4.5 Question 3

An electron is accelerated through a potential difference of 400 V. Determine its de Broglie wave length.

### 3.4.6 Answer 3

Kinetic energy gained by the electron (non-relativistic),  $T = \frac{p^2}{2m} = 400 \text{ eV}$

$$\therefore p = \sqrt{2mT}$$

$$\text{Mass of the electron} = 9.11 \times 10^{-31} \text{ kg}$$

$$\text{Charge of the electron} = 1.602 \times 10^{-19} \text{ Coulombs}$$

Hence, the linear momentum,

$$\begin{aligned}
 p &= \left[ (400 \times 1.602 \times 10^{-19} \text{ J}) \times (2 \times 9.11 \times 10^{-31} \text{ kg}) \right]^{1/2} \\
 &= 10.798 \times 10^{-24} \text{ kg.ms}^{-1} \\
 \text{de Broglie wave length } \lambda &= \frac{h}{p} = \frac{6.626 \times 10^{-34}}{10.798 \times 10^{-24}} = 0.6132 \times 10^{-10} \text{ m} \\
 &= 0.6132 \text{ \AA}
 \end{aligned}$$

### 3.4.7 Question 4

The energy of certain X-rays is found to be equal to that of a 1 KeV electron. Compare their wave lengths.

### 3.4.8 Answer 4

The Kinetic energy is:

$$T = \frac{p^2}{2m} = 1000 \text{ eV} = 1.602 \times 10^{-19} \times 10^3 \text{ J} = 1.602 \times 10^{-16} \text{ J}$$

According to de Broglie, the wave length of an electron is:

$$\begin{aligned}
 \lambda &= \frac{h}{p} = \frac{h}{\sqrt{2mT}} = \frac{6.626 \times 10^{-34} \text{ J.s}}{[2(9.11 \times 10^{-31} \text{ kg}) \times (1.602 \times 10^{-16} \text{ J})]^{1/2}} \\
 &= 0.39 \times 10^{-10} \text{ m} = 0.39 \text{ \AA}
 \end{aligned}$$

Energy of X-rays:  $E = h\nu = \frac{hc}{\lambda}$

$$\text{Or: } \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J.s})(3 \times 10^8 \text{ m.s}^{-1})}{1.602 \times 10^{-16} \text{ J}} = 12.408 \text{ \AA}$$

Hence,  $\frac{\text{wave length of X-rays}}{\text{de Broglie wave length of electron}} = \frac{12.408}{0.39} = 31.85$

The wave length of the X-rays is 31.85 times the de Broglie wavelength of the electron.

### 3.4.9 Question 5

The speed of an electron is found to be  $1 \text{ km.s}^{-1}$  within an accuracy of 0.02%. Calculate the uncertainty in its position.

### 3.4.10 Answer 5

The momentum of the electron:  $p = mv = (9.11 \times 10^{-31} \text{ kg})(1000 \text{ ms}^{-1})$

$$\% \text{ accuracy} = \frac{\Delta P \times 100}{P} = 0.02\%$$

$$\Delta P = \frac{0.02 \times 9.11 \times 10^{-31} \times 1000}{100} = 1.822 \times 10^{-31} \text{ kg.m.s}^{-1}$$

$$\Delta x; \frac{h}{4\pi\Delta P} = \frac{6.626 \times 10^{-34} \text{ J.s}}{4\pi \times 1.822 \times 10^{-31} \text{ kg.m.s}^{-1}} = 2.894 \times 10^{-4} \text{ m}$$

### 3.4.11 Question 6

In a hydrogen atom, the electron in the  $n = 2$  excited state remains there for  $10^{-8}$  seconds on an average before making a transition to the ground state ( $n = 1$ ). (a) Calculate the uncertainty in energy of the excited state. (b) What is the fraction of the transition energy? (c) Compute the width of wave length corresponding to this.

### 3.4.12 Answer 6

a)

$$\Delta E \times \Delta t \geq h$$

$$\Delta E \geq \frac{h}{\Delta t} = \frac{6.626 \times 10^{-34} \text{ J.s}}{10^{-8} \text{ s}} = 6.626 \times 10^{-26} \text{ J}$$

$$\text{Or } \frac{6.626 \times 10^{-26}}{1.602 \times 10^{-19}} \text{ eV} = 4.14 \times 10^{-7} \text{ eV}$$

b)

$$\text{Energy of } n = 2 \rightarrow n = 1 \text{ transition is } -13.6 \text{ eV} \left( \frac{1}{2^2} - \frac{1}{1^2} \right) = 10.2 \text{ eV}$$

$$\text{Fraction of energy} = \frac{\Delta E}{E} = \frac{4.14 \times 10^{-7}}{10.2} = 4.06 \times 10^{-8}$$



c)

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J.s}) (3 \times 10^8 \text{ m.s}^{-1})}{10.2 \times 1.602 \times 10^{-19} \text{ J}} = 1218 \text{ \AA}$$

$$\text{The spectral line width of this line} = \frac{\Delta\lambda}{\lambda} = \frac{\Delta\nu}{\nu} = \frac{\Delta E}{E}$$

$$\Delta\lambda = \frac{\Delta E \times \lambda}{E} = 4.06 \times 10^{-8} \times 1.218 \times 10^{-7} = 4.95 \times 10^{-7} \text{ \AA}$$

### 3.4.13 Question 7

Write down the normalized wavefunction if  $\psi(x) = A \exp(-kx^2)$ , where  $k$  and  $A$  are real constants over the entire domain.

### 3.4.14 Answer 7

$$\psi(x) = A \exp(-kx^2)$$

For the normalized wavefunction:

$$\int_{-\infty}^{+\infty} (A\psi^*) (A\psi) dx = 1$$

$$A^2 \int_{-\infty}^{+\infty} \exp(-2kx^2) dx = 1$$

But we know that  $\int_{-\infty}^{+\infty} \exp(-2kx^2) dx = \sqrt{\frac{\pi}{2k}}$

$$\text{Or } A = \left(\frac{2k}{\pi}\right)^{1/4}$$

$$\psi(x) = \left(\frac{2k}{\pi}\right)^{1/4} \exp(-kx^2)$$

**3.4.15 Question 8**

Given  $\psi(x) = A \sin(kx)$ . Find the eigenvalues of the operator  $\hat{O} = \frac{\partial^2}{\partial x^2}$ . Find out whether  $\hat{O} = \frac{\partial}{\partial x}$  is an eigenoperator.

**3.4.16 Answer 8**

$$\frac{\partial \psi(x)}{\partial x} = \frac{\partial [A \sin(kx)]}{\partial x} = Ak \cos(kx). \text{ This is not of the form } \hat{k}\psi(x) = k\psi(x)$$

$\therefore \frac{\partial}{\partial x}$  is not an eigenoperator for the function.

$$\frac{\partial^2 \psi(x)}{\partial x^2} = \frac{\partial^2 [A \sin(kx)]}{\partial x^2} = -k^2 A \sin(kx)$$

$\therefore \frac{\partial^2}{\partial x^2}$  is an eigenoperator with an eigenvalue of  $(-k^2)$  for the function.

**3.4.17 Question 9**

Find the voltage with which electrons in an electron microscope have to be accelerated to get a wavelength of 1 Å.

**3.4.18 Answer 9**

Let  $V$  be the voltage to be applied on electrons. Then the kinetic energy gained =  $eV$  Joules. ( $e = 1.602 \times 10^{-19}$  Coulombs). The de Broglie wavelength can be calculated from the relation:

$$\lambda = \frac{h}{p}. \quad (3.34)$$

Now the kinetic energy  $\frac{p^2}{2m} = eV$ . Or:

$$p = \sqrt{2meV} \quad (3.35)$$

From Eqs. (3.34) and (3.35), the de Broglie wavelength is:

$$\lambda = \frac{h}{\sqrt{2meV}} = 1 \text{ \AA}$$

Hence:

$$V = \frac{h^2}{2me\lambda^2} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2}{(1.602 \times 10^{-19}) \times 2 \times (9.11 \times 10^{-31} \text{ kg}) \times (1 \times 10^{-10} \text{ m})^2} \\ = 150 \text{ V}$$

### 3.4.19 Question 10

Calculate the minimum energy of an electron inside a hydrogen atom whose radius is  $0.53 \text{ \AA}$  using the uncertainty principle.

### 3.4.20 Answer 10

$$\Delta x = 5.3 \times 10^{-11} \text{ m}$$

$$\therefore \Delta p = \frac{\eta}{2\Delta x} \geq 9.9 \times 10^{-25} \text{ kg} \cdot \text{ms}^{-1}$$

$$\text{Kinetic energy of electron} = \frac{(\Delta p)^2}{2 \times 2\pi m} = \frac{(9.9 \times 10^{-25} \text{ kg} \cdot \text{ms}^{-1})^2}{2 \times 9.11 \times 10^{-31} \text{ kg}} \\ = 5.4 \times 10^{-19} \text{ J} \\ = 3.37 \text{ eV}$$

## 3.5 Exercises

1. Calculate the wavelength of an electron that has been accelerated through a potential of 100 million volts.
2. An electron has a speed of  $500 \text{ m s}^{-1}$  with an uncertainty of 0.02%. What is the uncertainty in locating its position?
3. The ionization energy of a hydrogen atom in the ground state is  $1312 \text{ kJ mol}^{-1}$ . Calculate the wavelength of radiation emitted when the electron in the hydrogen atom makes a transition from principal quantum level,  $n = 2$  to  $n = 1$ .

4. Calculate the de Broglie wavelength for an electron traveling at 1 percent of the speed of light.
5. Find the eigenfunctions of the momentum operator assuming that  $P'\phi = p\phi$ , where  $p$  is the momentum.
6. Assume that the Hamiltonian operator is invariant under time reversal. Prove that the wavefunction for a spin less non-degenerate system at any given instant of time can always be real.
7. The Hamiltonian operator for a spin 1 system is given by  $H = \alpha S_z^2 + \beta (S_x^2 - S_y^2)$ . Solve this equation to find the normalized energy states and eigenvalues. Is this Hamiltonian invariant under time reversal? How do the normalized eigenstates transform under time reversal?
8. Using uncertainty principle show that an electron can not be confined to the nucleus of the atom. (The typical radius of a nucleus =  $10^{-15}$  m).

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