



KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
M.Sc Chemistry – Syllabus

17CHP103

PHYSICAL CHEMISTRY- I:
QUANTUM CHEMISTRY AND GROUP THEORY

Semester-I
4H 4C

Instruction Hours/week:L: 4 T:0 P:0

arks: Internal:40 External: 60 Total:100

Scope

This course presents the Basic principles of quantum chemistry which involves the failure of classical mechanics, wave equations, approximation methods and basic concepts of Group Theory.

Programme Outcome

1. To study the fundamentals and applications of classical mechanics and quantum chemistry.
2. To understand the structure of an atom and different approximation methods.
3. To learn the concept of Group theory and their applications.

Programme Learning Outcomes

1. Understand the basic principles of quantum mechanics.
2. Understand the path integral representation of quantum mechanics.
3. Understand the operator formulation of quantum mechanics.
4. Understand the form and construction of relativistic wave equations.
5. Understand the Molecular geometry and Structure.
6. Understand the Vibrational modes of Molecular and identify the molecules.

UNIT – I

Failure of classical mechanics and the success of quantum theory in explaining black body radiation and photoelectric effect.

The time dependent and time independent Schrodinger equations - Born's interpretation of the wave function. Requirements of the acceptable wave function.

Algebra of operators. Sums and products of operators - commutator - linear operators- eigen functions and eigen values - correspondence between physical quantities in classical mechanics and operators in quantum mechanics - Hamiltonian operator - angular momentum operator. Quantization of angular momentum and its spatial orientation - average values - postulates of quantum mechanics.

UNIT – II

Particle in a one-dimensional box - quantization of energy - normalization of wave function - orthogonality of the particle in a one-dimensional box wave functions. Illustration of the uncertainty principle and correspondence principle with reference to the particle in a one-dimensional box - particle in a three dimensional box - separation of variables.

Solving of Schrodinger equation for one-dimensional harmonic oscillator. Harmonic oscillator model of a diatomic molecule. Illustration of the uncertainty principle and correspondence principle with reference to harmonic oscillator.

Solving of Schrodinger equation for a rigid rotor. Rigid rotor model of a diatomic molecule.

UNIT – III

Schrodinger equation for the H-atom (or H-like species)- separation of variables - energy levels. Radial distribution functions - orbitals and orbital shapes. Probability density and radial distribution functions.

Need for approximation methods. The perturbation theory- application of perturbation method to systems such as anharmonic oscillator and He-atom.

The variation method - application of variation method to systems such as anharmonic oscillator and He-atom.

UNIT – IV

Symmetry elements and symmetry operations - definition of identical and equivalent elements configurations - effect of performing successive operations commutative and non-commutative - inverse operations.

Groups and their basic properties - definition of a group - basic properties of a group-definition of abelian - cyclic- isomorphic, finite, infinite groups and subgroup. Symmetry classification of molecules into point groups-Schoenflies symbol (only-difference between point group and space group).

Matrices- Definition of matrix, square matrix, diagonal matrix, null matrix, unit matrix, row matrix, column matrix, symmetric matrix, skew symmetric matrix and conjugate matrix. Multiplication, commutative and non commutative-determination of inverse of a matrix, block multiplication of matrices-addition and subtraction of matrices.

Matrix notations for symmetry operations of C_{2v} and C_{3v} groups-construction of character tables for C_{2v} and C_{3v} point groups.

UNIT – V

Definition of reducible and irreducible representations - irreducible representations as orthogonal vectors - direct product rule, the great orthogonality theorem and its consequences - determinations of the characters for irreducible representation of C_{2v} and C_{3v} point groups using the orthogonality theorem.

Group theory and Vibrational spectroscopy - vibrational modes as basis for group representation - symmetry selection rules for IR and Raman spectra, Mutual exclusion principle - classification of vibrational modes.

SUGGESTED READINGS:

Text Books:

1. Prasad, R. K. (2014). *Quantum Chemistry* (II Edition). New Delhi: New Age International Publishers Pvt. Ltd.
2. Cotton, F. A. (2002). *Chemical Applications of Group Theory* (III Edition). Texas: A Wiley Inter Science Publication.
3. Chandra, A. K. (2012). *Quantum Chemistry* (IV Edition). New Delhi: Tata McGraw – Hill Publishing Company Ltd.
4. House, J. E. (2013). *Fundamental of Quantum Chemistry* (II Edition). New Delhi: Academic Press.
5. S.Swarnalakshmi T.Saroja, R.M. Ezhilarasi, 2009, A Simple approach to group theory in chemistry, University Press Pvt., Ltd., New Delhi.

Reference Books:

1. Raman, K.V. (2002). *Group Theory and its Applications to Chemistry*. New Delhi: Tata McGraw Publishing Company.
2. Puri, B. R., Sharma, L. R., & Pathania, M. S. (2013). *Principles of Physical Chemistry* (46th Edition). Jalandar: Vishal Publishing Co.
3. Veera Reddy, K. (2009). *Symmetry and Spectroscopy of Molecules*. New Delhi: New Age International Pvt. Ltd.
4. Atkins, P., & De Paula, J. (2014). *Atkins Physical Chemistry* (X Edition). Oxford: Oxford University Press.



LECTURE PLAN

Year : I

T2: Puri Sharma and Pathania, 2013, Elements of Physical Chemistry, Vishal Publishing Co., New Delhi

Unit II**Total no. of hour's: 12**

S.No	Lecture Hour	Topic	Reference
1.	1	Particle in a one-dimensional box	T1: 39-41
2.	1	quantization of energy - normalization of wave function -	T1: 42-43
3.	1	orthogonality of the particle in a one-dimensional box wave functions.	T1: 43
4.	1	Illustration of the uncertainty principle and correspondence principle with reference	T1:43-45; T2: 640-641
5.	1	The particle in a one-dimensional box	
6.	1	particle in a three dimensional box - separation of variables.	T1:47-49; T2: 644-645
7.	1	Solving of Schrodinger equation for one-dimensional harmonic oscillator.	T1:82-84
8.	1	Harmonic oscillator model of a diatomic molecule.	T2: 645-646
9.	1	Illustration of the uncertainty principle and correspondence principle with reference to harmonic oscillator.	T1:84-87; T2: 646
10.	1	Solving of Schrodinger equation for a rigid rotor	T1: 52-55
11.	1	Rigid rotor model of a diatomic molecule.	T1:52-55
12.	1	Revision & Discussion of possible questions	

Textbook

T1: A.K.Chandra, 2010, Introductory quantum Chemistry, Tata McGraw Hill Education Pvt., Ltd, New Delhi

T2: Puri Sharma and Pathania, 2013, Elements of Physical Chemistry, Vishal Publishing Co., New Delhi

Unit III**Total no. of hour's: 12**

S.No	Lecture Hour	Topic	Reference
1.	1	Schrodinger equation for the H-atom (or H-like species)	T1: 89-90; T2: 647-649
2.	1	separation of variables - energy levels	T1: 91; T2: 648
3.	1	Radial distribution functions	T1: 91-93
4.	1	Orbitals and orbital shapes	T2: 651-653
5.	1	Probability density and radial distribution functions.	T1:94-97
6.	1	Need for approximation methods	T1: 109-100
7.	1	The perturbation theory	T1: 111
8.	1	Application of perturbation method to systems such as anharmonic oscillator.	T1: 115-116
9.	1	Anharmonic oscillator of He atom	T1: 117
10.	1	The variation method - application of variation method	T1: 115-117
11.	1	application of variation method to systems such as anharmonic oscillator and He-atom.	T1: 118-120
12.	1	Recapitulation and discussion of important questions	

Textbook

T1: A.K.Chandra, 2010, Introductory quantum Chemistry, Tata McGraw Hill Education Pvt., Ltd, New Delhi

T2: Puri Sharma and Pathania, 2013, Elements of Physical Chemistry, Vishal Publishing Co., New Delhi

Unit IV**Total no. of hour's: 13**

S.No	Lecture Hour	Topic	Reference
1.	1	Symmetry elements and symmetry operations	T1:288-291
2.	1	Definition of identical and equivalent elements configurations	T1: 291-293
3.	1	The operations commutative and non-commutative - inverse operations.	T1: 294-295
4.	1	Groups and their basic properties - definition of a group	T1: 295-302
5.	1	basic properties of a group-definition of abelian – non-abelian	T1:303
6.	1	Cyclic- isomorphic, finite, infinite groups and subgroup.	T1: 304
7.	1	Symmetry classification of molecules into point groups-Schoenflies symbol	T1:304-306
8.	1	Matrices- Definition of matrix, square matrix, diagonal matrix, null matrix, unit matrix.	T2: 62-63
9.	1	Row matrix, column matrix, symmetric matrix, skew symmetric matrix and conjugate matrix.	T2: 63-64
10.	1	Multiplication, commutative and non commutative-determination of inverse of a matrix	T1: 306-307
11.	1	block multiplication of matrices-addition and subtraction of matrices.	T1: 308-309
12.	1	Matrix notations for symmetry operations of C_{2v} and C_{3v} groups. construction of character tables for C_{2v} and C_{3v} point groups.	T1: 309-310
13.	1	Revision & Discussion of important questions	

Textbook

T1: A.K.Chandra, 2010, Introductory quantum Chemistry, Tata McGraw Hill Education Pvt., Ltd, New Delhi

T2: S.Swarnalakshmi T.Saroja, R.M. Ezhilarasi, 2009, A Simple approach to group theory in chemistry, University Press Pvt., Ltd., New Delhi.

Unit V**Total no. of hour's: 13**

S.No	Lecture Hour	Topic	Reference
1.	1	Definition of reducible and irreducible representations	T1:310-311
2.	1	irreducible representations as orthogonal vectors	T2:82-83
3.	1	direct product rule, the great orthogonality theorem and its consequences	T2:83-85
4.	1	Determinations of the characters for irreducible representation of C_{2v} point groups using the orthogonality theorem.	T1:311-315
5.	1	irreducible representation of C_{3v} point groups	T1:312-315
6.	1	Group theory and Vibrational spectroscopy - vibrational modes as basis for group	T2:117-118
7.	1	symmetry selection rules for IR and Raman spectra	T2:119-123
8.	1	Mutual exclusion principle - classification of vibrational modes.	T2:119-121
9.	1	Group theory and dipole moment	T2:60
10.	1	Revision & Discussion of important questions	
11.	1	Discussion of end semester questions	
12.	1	Discussion of end semester questions	
13.	1	Discussion of end semester questions	

Textbook

T1: A.K.Chandra, 2010, Introductory quantum Chemistry, Tata McGraw Hill Education Pvt., Ltd, New Delhi

T2: S.Swarnalakshmi T.Saroja, R.M. Ezhilarasi, 2009, A Simple approach to group theory in chemistry, University Press Pvt., Ltd., New Delhi.

UNIT – I
Quantum Mechanics

Failure of classical mechanics and the success of quantum theory in explaining black body radiation and photoelectric effect.

The time dependent and time independent Schrodinger equations - Born's interpretation of the wave function. Requirements of the acceptable wave function.

Algebra of operators. Sums and products of operators - commutator - linear operators- eigen functions and eigen values - correspondence between physical quantities in classical mechanics and operators in quantum mechanics - Hamiltonian operator - angular momentum operator. Quantization of angular momentum and its spatial orientation - average values - postulates of quantum mechanics.

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– **Quantum mechanics**

is the foundation of all modern fields of sciences, including chemistry, biology, and material sciences; it is the ONLY way to TRULY understand

Structures and properties matters

Nature of atoms, chemical bonds, and molecules

Intermolecular forces (hydrogen bonds and van der Waals forces)

Enzymology, proteinomics, and genomics

Nanoscience and material science

Property of electromagnetic radiation (such as light)

Matter interaction with external electromagnetic fields

– **Quantum chemistry** is built up on the principles of quantum mechanics, and provides further the

molecular understanding on the structures and properties of chemical compounds, materials, and biological processes

– **Statistical mechanics** rests on the foundation of quantum mechanics (including quantum chemistry) and provides the basis of thermodynamics

THE ORIGINS OF QUANTUM MECHANICS

Many experimental evidences merged around 1900, showing the **fundamental failure of (Newtonian)**

classical mechanics,

including even some basic (daily-life) concepts/pictures about matter and light

- Electron in a hydrogen atom:

$$\text{Kinetic energy} = \frac{1}{2m_e}(p_x^2 + p_y^2 + p_z^2); \quad \text{Potential energy } V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Classical mechanics: Total energy = kinetic energy + potential energy, which can be any value.

Experimental observation: The optical spectrum of H consists of series of **discrete** lines.

Question/Suggestion: Does the energy of electron in H take **discrete** values ?

- **Harmonic oscillator** systems (e.g. vibration motion), *with the same question/suggestion*

$$\text{Kinetic energy} = \frac{p^2}{2m}; \quad \text{Potential energy } V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2$$

Classical mechanics: 1) Vibration energy $E_{\text{vib}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$ can take *any value* (≥ 0)

2) Thermal average $\langle E_{\text{vib}} \rangle = k_B T$ (**equipartition theorem**)

Systems Relating to Harmonic Oscillators

- (i) Heat capacity $C_{m,V}$ of monatomic solid (contributed only by the **oscillatory motion** of atoms around their equilibrium lattice positions)

$$\Rightarrow C_{m,V} = N_A \left(\frac{\partial \langle E_{\text{osc}} \rangle}{\partial T} \right)_V$$

Classical mechanics: $C_{m,V} = 3R$ at any T ($R = N_A k_B$ the gas constant)

Experiments: $C_{m,V} \rightarrow 0$ as $T \rightarrow 0$

Does the energy of an oscillation motion take **discrete** values ?

(ii) Blackbody radiation (radiation field is just a collection of electromagnetic **oscillators**; to be continued)

The density of states of blackbody radiation: $\rho(\lambda, T) = \frac{8\pi}{\lambda^4} \langle E_{osc} \rangle$

Classical mechanics: $\rho(\lambda, T) = \frac{8\pi}{\lambda^4} k_B T$, fails total at small λ . **Ultraviolet catastrophe !**

Experiments: $\rho(\lambda, T) \rightarrow 0$ as $\lambda \rightarrow 0$, at any finite temperature T .

(iii) Light (being an electromagnetic field) is a **harmonic oscillating wave** traveling through space

The most important property of a wave is the **interference** phenomenon

Basic relations and knowledge (speed c , wavelength λ , frequency ν)

1) $\lambda \nu = c$

2) circular frequency $\omega = 2\pi\nu$

3) **wavenumber** $\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$ (unit: cm^{-1})

4) Light as an electromagnetic field, $E(x, t) = \exp(ik_x x - i\omega t)$ or $\vec{E}(\vec{r}, t) = \exp(i\vec{k} \cdot \vec{r} - i\omega t)$

5) Wavevector $\vec{k} = \begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix} = (k_x, k_y, k_z)^T$

-- direction of \vec{k} = direction of light propagation

-- magnitude $k = \sqrt{k_x^2 + k_y^2 + k_z^2} = \frac{2\pi}{\lambda} = \omega / c$

Fundamental Constant in Quantum Mechanics:

Planck constant $h \equiv 6.626 \times 10^{-34} \text{ J s}$; also $\hbar \equiv h/(2\pi) = 1.055 \times 10^{-34} \text{ J s}$

- In his study of blackbody radiation, Max Planck (1900) proposed that the permitted energies of an electromagnetic oscillator of frequency ν are $E = n h \nu$, $n = 0, 1, 2, \dots$, the single **revolutionary** assumption led to a complete satisfactory interpretation of blackbody radiation experiment
- This result suggests an electromagnetic radiation (wave) consists of $n = 0, 1, 2, \dots$ particles, called **photons**, each photon having an energy of $h\nu$
- With the concept of photon, Einstein (1905) successfully explained the **photoelectric effect** (§ 8.2(a))
- Since then, the Planck constant becomes a basic ingredient of quantum mechanics, **containing in all quantum equations, laws, relations, and consequences**
- Planck constant plays no role in classical world; all quantum theory approaches to the classical physics by setting the limit of $h \rightarrow 0$. Therefore, quantum mechanics is said to generalize and supersede the classical mechanics, and classical mechanics would still be useful if the value of Planck constant could be considered to be negligibly small

Blackbody Radiation (1900, Max Planck)

- i. Radiation wave is an electromagnetic (light) wave, created by electric *oscillator* at certain frequency ($\nu = c/\lambda$)
- ii. Blackbody is an ideal (theoretical) object that absorbs all the electromagnetic waves falling on it
- iii. Blackbody radiation concerns about the energy (power) profile of the radiation wave emitted from a blackbody at given temperature (i.e. in thermal equilibrium with radiation)
- iv. Radiation fields inside blackbody cavity are all **standing waves**. As a result, $\frac{\# \text{ modes in wavelength}}{\text{cavity volume}} = \frac{8\pi}{\lambda^4}$

- Energy spectral density $\rho(\lambda, T) = \frac{8\pi}{\lambda^4} \langle E_{osc} \rangle$

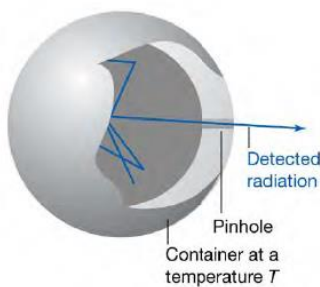


Fig. 8.4

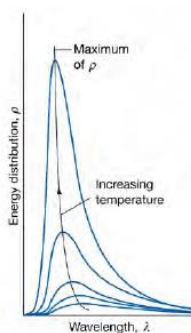


Fig. 8.3

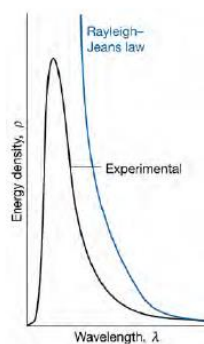
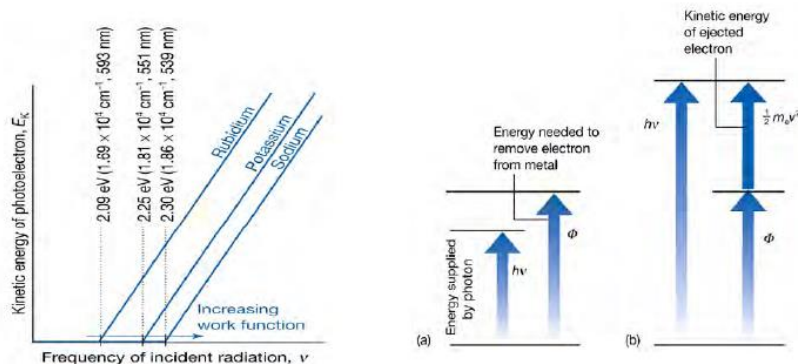


Fig. 8.6

Photoelectric Effect (1905, Einstein)

When a metal exposed to a light of frequency ν , free electrons can be ejected only when ν is large enough (i.e., short wavelength) such that $h\nu \geq \Phi$, where Φ is the so-called “work function” characterizing how strong an electron is bound to the metal. The ejected free electron is found to have the kinetic energy of

$$E_{\text{kinetic}} = h\nu - \Phi, \text{ which does not depend on the light intensity.}$$



- Quantization**

- 1) The dynamic observables (i.e., any functions of coordinates and momentums in classical mechanics) are said being **quantized**, if possible results of *individual* measurement on them are of all or partly discrete values
- 2) Quantization occurs in not only matter (such as electron, atom, molecules etc) but also for light, typically concerning about the total energy, angular momentum, and spin
- 3) There are simple rules established, namely Quantum Mechanics (QM) – thanks to Erwin Schrödinger (1925) and to Werner Heisenberg (1926) – to describe the quantization phenomena (§ 8.3)
- 4) A quantum system is completely described by the wavefunction that is governed by Schrödinger equation, which goes also with **Born interpretation** of wavefunction (§ 8.4), as for **wave-particle duality** (§ 8.2)

- **Uncertainty principle**

In classical physics the observables characterizing a given system are assumed to be simultaneously measurable (in principle) with arbitrarily small error. For instance, the position and momentum of a Newtonian particle can be precisely characterized at both the initial time and any time later as the classical trajectory. As a consequence, classical particle can have any (continuous) values of energy. However, quantum mechanics leads to the following uncertainty relation (Heisenberg, 1926),

$$\Delta x \Delta p_x \geq \hbar/2$$

Therefore, if the momentum of the particle at the x -direction is measured accurately with no uncertainty ($\Delta p_x = 0$), its x -position will have to be completely random ($\Delta x \rightarrow \infty$), spreading all over of $-\infty < x < \infty$.

Another important uncertainty relation is between energy and time, $\Delta E \Delta t \geq \hbar/2$

- **Zero-point energy**

The lowest permitted energy of a quantum system is usually higher than the minimum potential energy due to the uncertainty principle. The lowest permitted energy above the potential minimum is called the zero-point energy. In contrast, the classically permitted lowest energy rests at the potential minimum. Zero-point energy plays the crucial role in chemistry, especially in reactions related to electron and/or hydrogen transfer dynamics

- **Wave-particle duality**

Einstein's idea of photon (to explain the photoelectric effect) that $E = h\nu$ gave rise of the particle property of electromagnetic wave (light). Together with his famous $E = mc^2$, the momentum of light wave, $p = mc$, can then be related to the light wavelength $\lambda = c/\nu$ as

$$p = h/\lambda$$

The above relation was experimentally verified in the Compton effect (1922), wherein the wavelengths of x-rays are lengthened (while the electron gains momentum) by scattering from free electrons. The change in wavelength is predicted quantitatively, assuming the scattering results from elastic collisions between photons and electrons.

In 1924, Louis de Broglie suggested that not only photons, any particle traveling with a linear momentum p , should exhibit wave property with wavelength

$$\lambda = h/p$$

The wave property of particles, together with the de Broglie relation, were demonstrated first in electron diffraction experiments (Clinton J. Davisson and Lester H. Germer, 1927), and later also with other particles (neutron, H atom, He atom, and H₂ molecule) as diffraction beams, even with C₆₀ molecules (Arndt et al., *Nature*, **401** (1999) 680).

NOTE: Energy in terms of wave property

Often the discrete energies in matter (atoms, molecules, and solids, etc) are detected with light or other forms of electromagnetic field by either absorption or emission a photon. The energy conservation requires that $\Delta E = h\nu$, where ΔE denotes the energy change in the matter system due to it absorbs and emits a photon of frequency ν . As a result, the value of energy can be specified in terms of

- (a) frequency: $1 \text{ Hz} \Leftrightarrow 6.626 \times 10^{-34} \text{ J}$
 (b) wavenumber ($1/\lambda = \nu/c$): $1 \text{ cm}^{-1} \Leftrightarrow 1.986 \times 10^{-23} \text{ J}$

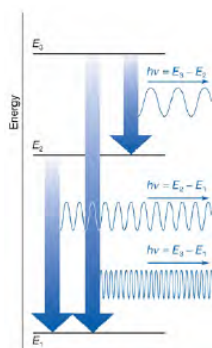


Fig. 8.12

SCHRÖDINGER EQUATION AND QUANTUM MECHANICS

In 1926, Erwin Schrödinger proposed that the quantum state of matter is described by the so-called wave function $\Psi(\mathbf{r}, t)$, which in general is a complex function of the matter's coordinates and time, and its evolution is governed by (**Schrödinger equation**)

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H} \Psi(\mathbf{r}, t)$$

Here, \hat{H} is an **operator** that closely relate to the classical Hamiltonian; or, loosely speaking, the energy expression, $H = \text{kinetic energy} + \text{potential energy}$:

$$\hat{H} \equiv \text{kinetic energy operator} + \text{potential energy operator}$$

➤ **Rule of Writing Operator** (in real space or coordinate space)

	Classical variable	Quantum operator	Operator in real space
Coordinator	x	\hat{x}	x
Momentum	p_x	\hat{p}_x	$\frac{\hbar}{i} \frac{\partial}{\partial x}$

- **Hamiltonian Operator** (e.g. a particle of mass m moving in one-dimensional space)

	Classical expression	Operator in real space
Kinetic energy	$\frac{p^2}{2m}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$V(x)$
Hamiltonian	$\frac{p^2}{2m} + V(x)$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$

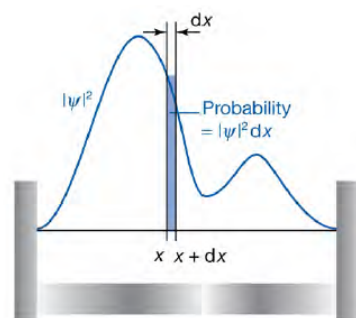
- **Schrödinger Equation for 1D-System**

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

- **Born Interpretation**

$\Psi(x,t)$ is a complex function describing the **probability wave** that

$$|\Psi(x,t)|^2 dx \propto \text{probability of finding the particle within } [x, x + dx] \text{ at time } t$$



- **Property of Wave Function**

(1) Single-valued (2) Both $\Psi(x,t)$ and $\partial\Psi(x,t)/\partial x$ continuous (3) Integrable

- $\lambda\Psi(x,t)$ describes the same quantum state of $\Psi(x,t)$, where λ is an complex constant

- **Normalized Wave Function**

$$\frac{\Psi(x,t)}{\sqrt{\int_{\text{all space}} |\Psi(x,t)|^2 dx}} \xrightarrow{\text{normalization}} \Psi(x,t)$$

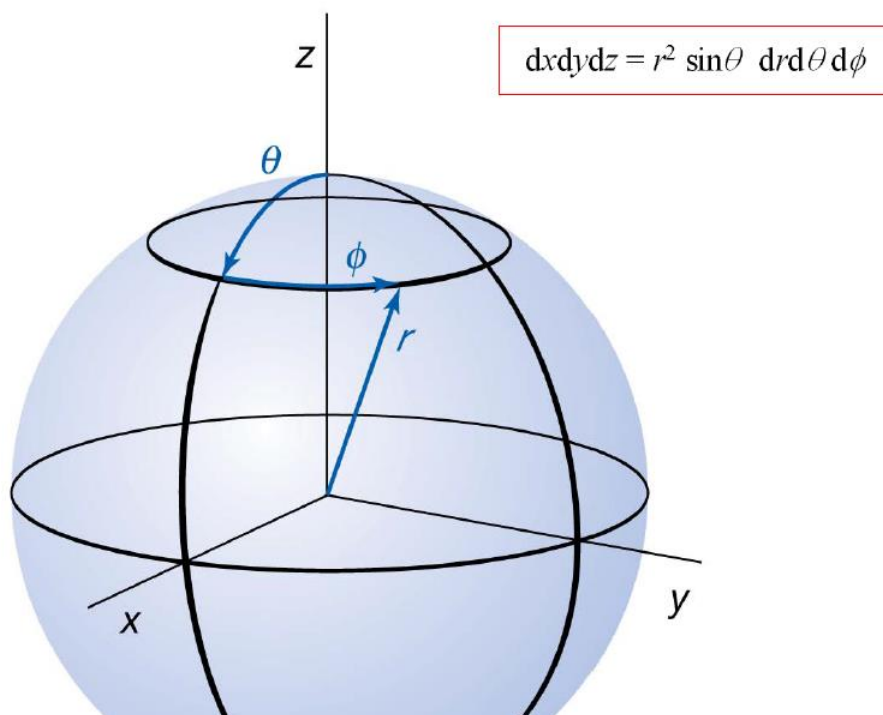
The normalized $\Psi(x,t)$ satisfies $\int_{\text{all space}} |\Psi(x,t)|^2 dx = 1$

- **Property of Schrödinger Equation and Wave Functions**

(i) If $\Psi_1(x,t)$ and $\Psi_2(x,t)$ are solutions to the Schrödinger equation, $c_1\Psi_1(x,t) + c_2\Psi_2(x,t)$ (which is called linear combination or **coherent superposition** of the composite wavefunctions) must also satisfy the same Schrödinger equation, where c_1 and c_2 are arbitrary complex numbers.

(ii) **Quantum interference (constructive vs. destructive inference)**

Consider, for example, the plane waves, $\Psi_{\rightarrow} = e^{i2\pi(x/\lambda - \nu t)}$ and $\Psi_{\leftarrow} = e^{-i2\pi(x/\lambda + \nu t)}$, where λ and ν are the wavelength and frequency of the plane wave. (a) Show that both Ψ_{\rightarrow} and Ψ_{\leftarrow} are solutions to the Schrödinger equation with $V(x) = 0$; (b) Show that the standing wave $\Psi_{\rightarrow} + \Psi_{\leftarrow} = 2\cos(2\pi x/\lambda)e^{-i2\pi\nu t}$ is also a solution to the same Schrödinger equation; (c) Evaluate $|\Psi_{\rightarrow}|^2$, $|\Psi_{\leftarrow}|^2$, and $|\Psi_{\rightarrow} + \Psi_{\leftarrow}|^2$, and make comments on constructive and destructive interferences.



➤ Stationary Schrödinger Equation versus Time-dependent Solution

The steps to the formal solution to $i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H}\left(x, \frac{\hbar}{i} \frac{\partial}{\partial x}\right) \Psi(x,t)$

- (i) Consider first the space-time factorized form of wave function: $\Psi(x,t) \equiv \psi(x)\eta(t)$

Schrödinger equation becomes now $i\hbar \psi(x) \frac{\partial \eta(t)}{\partial t} = \left[\hat{H}\left(x, \frac{\hbar}{i} \frac{\partial}{\partial x}\right) \psi(x) \right] \eta(t)$.

Now dividing $\psi(x)\eta(t)$ to both sides $\Rightarrow i\hbar \frac{1}{\eta(t)} \frac{\partial \eta(t)}{\partial t} = \frac{1}{\psi(x)} \left[\hat{H}\left(x, \frac{\hbar}{i} \frac{\partial}{\partial x}\right) \psi(x) \right]$, which must be a

constant E to be determined that depends neither x nor t . We have therefore

$$i\hbar \frac{\partial \eta(t)}{\partial t} = E\eta(t) \quad \text{and} \quad \hat{H}\left(x, \frac{\hbar}{i} \frac{\partial}{\partial x}\right) \psi(x) = E\psi(x)$$

\Downarrow solution

\Downarrow abbreviated as

$$\eta(t) = \exp(-iEt/\hbar)$$

$$\boxed{\hat{H}\psi = E\psi} \text{ also called Schrödinger equation (SE)}$$

- (ii) The time-independent SE determines **both the permitted energy E value**, which often turns out to be quantized and thus denoted as E_n with n the quantized number, **and its associated n^{th} stationary wave function ψ_n** . Together with (i), we conclude that $\{\Psi_n(x,t) = \exp(-iE_n t/\hbar) \psi_n(x)\}$ constitute the set of solutions to the time-dependent SE (assuming we have solved all E_n and ψ_n for the given \hat{H})

(iii) The general solution to the time-dependent SE (superposition principle):

$$\Psi(\mathbf{r}, t) = \sum_{\text{all } n} c_n e^{-iE_n t / \hbar} \psi_n(\mathbf{r}), \text{ where } c_n \text{ is complex coefficient}$$

(iv) $\Psi(\mathbf{r}, t)$ is normalized if $\psi_n(\mathbf{r})$ is normalized and $\sum_n |c_n|^2 = 1$

➤ **Interpretation of E_n , $\psi_n(\mathbf{r})$, and $\Psi(\mathbf{r}, t)$**

- E_n : Eigenenergy – the permitted energy value (real) if a measurement is performed
- $\psi_n(\mathbf{r})$: Eigenstate wave function – the stationary wave function being of defined energy value of E_n
- Both E_n and ψ_n are determined by the system Hamiltonian operator \hat{H} via $\hat{H} \psi_n = E_n \psi_n$, which is also called the eigenequation of \hat{H}
- For the system with wave function $\Psi(\mathbf{r}, t) = \sum_n c_n(t) \psi_n(\mathbf{r})$, where $c_n(t) \equiv c_n e^{-iE_n t / \hbar}$, a single energy

measurement will only have a permitted value $\in \{E_n\}$, and the probability of obtaining the value E_n is $|c_n(t)|^2$ if Ψ and all ψ_n are normalized

- **Expectation or mean value of energy and other dynamical variables in general**

For normalized Ψ and ψ_n : $\langle E \rangle = \sum_n |c_n|^2 E_n$. This is the same as

$$\langle E \rangle = \frac{\int_{\text{all space}} \Psi^*(\mathbf{r}, t) [\hat{H} \Psi(\mathbf{r}, t)] d\mathbf{r}}{\int_{\text{all space}} \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r}}$$

More generally, we have

$$\langle A \rangle = \frac{\int_{\text{all space}} \Psi^*(\mathbf{r}, t) [\hat{A} \Psi(\mathbf{r}, t)] d\mathbf{r}}{\int_{\text{all space}} \Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) d\mathbf{r}} \quad (\text{to be proved in L_Notes2})$$

State is Described by a Wavefunction

Quantum Mechanics uses a wavefunction to describe the state of matter. In principle, the wavefunction is not a direct observable. It describes the state in which the matter resides in mathematical terms. From it we can derive physical observables such as energy and momentum indirectly. To find these properties, we have to operate with an 'operator' onto the wavefunction to get the desired information out.

Operators and Wavefunctions

An operator $\hat{\Omega}$ performs a mathematical operation onto a function. An example is $\hat{\Omega} = \frac{d}{dx}$, which means: 'take the derivative to x of the function that follows'. A special case occurs when the operator operates on a function which yields a function proportional to the original:

$$\begin{aligned}\hat{\Omega}f &= \omega f \\ \frac{d}{dx}e^{ax} &= a \cdot e^{ax}\end{aligned}$$

In other words, operating $\hat{\Omega}$ onto f yields the same function f multiplied by a constant ω . We define:

$$\begin{aligned}\hat{\Omega} &= \text{operator} \\ f &= \text{eigenfunction} \\ \omega &= \text{eigenvalue}\end{aligned}$$

Operators may have more than one eigenfunction, each associated with an eigenvalue:

$$\hat{\Omega}f_n = \omega_n f_n$$

So more generally, operators may have a set of eigenfunctions. All the possible eigenfunctions of a given operator together is what we call a *complete set*. These sets play a central role in quantum mechanics, as we will see.

Orthogonality. Eigenfunctions f_n in the complete set are orthogonal. This implies that the overlap integral of two wavefunctions f_n and f_m taken over whole space is zero:

$$S_{\text{overlap}} = \int_{-\infty}^{\infty} f_n f_m^* dV = 0$$

This orthogonality is much similar to the orthogonality of vectors such as the orthogonal vectors (x, y, z) that define Cartesian space. The functions in a complete set are therefore often said to span a complete (multidimensional) space as well. The overlap integral of a (wave)function f_n with itself gives a finite value (see Born postulate for wavefunctions). If the functions are **normalized**, this overlap integral yields 1:

$$\int f_n f_n^* = \int |f_n|^2 = 1$$

Operator Forms

Important operators are the energy \hat{H} , position \hat{x} , and momentum \hat{p} operators. All these operators yield physical observables when operating onto a wavefunction. What is the mathematical form of the operators? In position (x) space, the operators are taking the following form:

$$\begin{aligned}\hat{x} &= x \cdot \quad (\text{multiply by } x) \\ \hat{p}_x &= \frac{\hbar}{i} \frac{\partial}{\partial x} \\ \hat{H} &= \hat{T} + \hat{V} = \frac{\hat{p}_x^2}{2m} + \hat{V} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}\end{aligned}$$

The operator \hat{V} is the operator for the potential energy. For example, for a coulomb potential it is given by:

$$\hat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}.$$

In three dimensions the Hamiltonian assumes the form:

$$\hat{H} = -\frac{\hbar^2}{2m} \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}$$

Alternatively, we could have expressed the operators in momentum (p) space. The position, momentum and energy operators then assume the forms:

$$\begin{aligned}\hat{x} &= -\frac{\hbar}{i} \frac{\partial}{\partial p} \\ \hat{p}_x &= p \cdot \\ \hat{H} &= \hat{T} + \hat{V} = \frac{p^2}{2m} + \hat{V}\end{aligned}$$

Commutation Relations

Operators operate on the function to the right. Hence, a product of two operators should be read as follows:

$$\hat{A}\hat{B}f = \hat{A}(\hat{B}f)$$

where $(\hat{B}f)$ is the new function for \hat{A} to operate on. Consequently, the product operator $\hat{A}\hat{B}$ is not necessarily the same as the operator $\hat{B}\hat{A}$. We now define the commutator of \hat{A} and \hat{B} :

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

The operators commute if

$$[\hat{A}, \hat{B}] = 0$$

If this condition does not hold, the operators are non-commuting. It can be shown quite easily that operators that share the same set of eigenfunctions, commute. We then have:

$$\begin{aligned}\hat{A}f &= af \\ \hat{B}f &= bf\end{aligned}$$

and thus

$$\begin{aligned}[\hat{A}, \hat{B}]f &= \hat{A}(\hat{B}f) - \hat{B}(\hat{A}f) \\ &= b\hat{A}f - a\hat{B}f \\ &= (ba - ab)f \\ &= 0\end{aligned}$$

Operators do not always share the same set of eigenfunctions. If they don't, the operators are non-commuting. An important example are the position and the momentum operators:

$$\begin{aligned}[\hat{x}, \hat{p}]f &= x \cdot \frac{\hbar}{i} \frac{\partial}{\partial x} f - \frac{\hbar}{i} \frac{\partial}{\partial x} \cdot x \cdot f \\ &= \frac{\hbar}{i} x \cdot \frac{\partial f}{\partial x} - \left(\frac{\hbar f}{i} + x \cdot \frac{\hbar}{i} \frac{\partial f}{\partial x} \right) \\ &= i\hbar \cdot f\end{aligned}$$

from which we recognize

$$[\hat{x}, \hat{p}] = i\hbar$$

this result is tightly connected to Heisenberg's Uncertainty Principle, and relates to the statement that position and momentum of a small particle cannot be determined with great precision simultaneously. Instead, there is an uncertainty of the order of \hbar between the operators.

Wave function

The wavefunction describes all the properties of a quantum mechanical system. It is, however, a mathematical construct. What is its physical meaning? The following section sheds light on the meaning of the wavefunction and the central equation in quantum mechanics: the Schrodinger equation.

- The state of a system is fully described by a wavefunction $\Psi(r_1, r_2, \dots, t)$

The wavefunction can encompass the state of multiple particles (1, 2...) in a system, such as a nucleus with its many electrons. The **total wavefunction** represents the state of the **whole system**. Remember that a wavefunction can be described as a weighed sum of a complete set of eigenfunctions ϕ_n of an operator:

$$\Psi(r) = \sum_n c_n \phi_n(r)$$

Wavefunctions are often labeled as $\Psi_{a,b,..}$ with quantum numbers ($a, b, ..$), which denote the different quantized states of the system. What is the

The probability that a particle will be found in volume element dV is proportional to $|\Psi(r)|^2$

This postulate is known as the Born interpretation of the wavefunction. In other words, the wavefunction is a probability amplitude and its square modulus a probability density. Born's interpretation of the wavefunction is based on the notion that particle must be somewhere in space, so that the overlap integral of the wavefunction with itself must be finite:

$$\int |\Psi(r)|^2 dV < \infty$$

Hence, the wavefunction should be square integrable. For normalized wavefunctions we get:

$$\int |\Psi(r)|^2 dV = 1$$

which means that if one attempts a measurement over whole space, the chance of finding the particle is one. This postulate also reinforces the meaning of the coefficient c_n . When we write the total wavefunction as $\Psi = \sum_n c_n \phi_n$, we have:

$$\begin{aligned} |\Psi|^2 &= \left(\sum_n c_n \phi_n \right)^* \left(\sum_m c_m \phi_m \right) \\ &= \sum_{n,m} c_n^* c_m \phi_n^* \phi_m \end{aligned}$$

and thus

$$\begin{aligned} \int |\Psi|^2 dV &= \sum_{n,m} c_n^* c_m \int \phi_n^* \phi_m dV \\ &= \sum_{n,m} c_n^* c_m \delta_{n,m} \\ &= \sum_n |c_n|^2 \end{aligned}$$

For normalized wavefunctions we get

$$\sum_n |c_n|^2 = 1$$

In other words, $|c_n|^2$ is the probability that the system is in a particular eigenstate ϕ_n . The probability that the system resides in the collection of all the available eigenstates, which is the sum over all $|c_n|^2$, is 1. This is equivalent to saying that a sampling over the whole of ' ϕ_n -space', must give the probability one, because the system has to be somewhere in this space.

The Schrödinger Equation

The wavefunction $\Psi(r, t)$ fully describes a system in space and time. The full evolution of the wavefunction is found from the **time-dependent Schrödinger Equation**:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

Here \hat{H} is the Hamiltonian, the energy operator:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V}_x$$

We can separate the time-dependent Schrödinger equation in a space-dependent and a time-dependent part. Let's write the wavefunction as:

$$\Psi(x, t) = \psi(x)\theta(t)$$

We now plug this into the Schrödinger Equation:

$$\begin{aligned} i\hbar \cdot \psi(x) \frac{\partial \theta(t)}{\partial t} &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} \cdot \theta(t) + \hat{V}_x \cdot \psi(x)\theta(t) \\ i\hbar \cdot \frac{1}{\theta(t)} \frac{\partial \theta(t)}{\partial t} &= -\frac{\hbar^2}{2m} \cdot \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}_x \end{aligned}$$

Now comes the trick. Each side depends on a different variable, while they equal each other at all times. Hence, each side equals a constant:

$$\begin{aligned} i\hbar \cdot \frac{1}{\theta(t)} \frac{\partial \theta(t)}{\partial t} &= E \\ -\frac{\hbar^2}{2m} \cdot \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}_x &= E \end{aligned}$$

which gives

$$\begin{aligned} i\hbar \frac{\partial \theta(t)}{\partial t} &= E\theta(t) \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}_x &= E\psi(x) \Rightarrow \hat{H}\psi(x) = E\psi(x) \end{aligned}$$

The solution of the first, time-dependent equation is:

$$\theta(t) \propto e^{-iEt/\hbar}$$

The solution of the second, time-independent Schrödinger equation is the stationary wavefunction $\psi(x)$:

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

We immediately recognize that this equation is an eigenvalue equation with operator \hat{H} , eigenfunctions Ψ , and eigenvalues E . The values for E thus correspond to the energy of the system. The total wavefunction can now be written as:

$$\Psi(x, t) = \psi(x) \cdot e^{-iEt/\hbar}$$

The wavefunction has thus a space-dependent amplitude and time-dependent phase. Note that in this formalism the phase has no influence on the probability density of a particle at any time, as

$$|\Psi(x, t)|^2 = \left(\psi(x)e^{-iEt/\hbar}\right) \cdot \left(\psi^*(x)e^{iEt/\hbar}\right) = \psi^*(x)\psi(x) = |\psi(x)|^2$$

Summary

We can find the wavefunction of a system by finding the eigenfunctions of the Hamiltonian. The corresponding eigenvalues give the permissible energy levels of the system. In summary we have:

Time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \hat{H} \Psi(x, t)$$

Time-independent Schrödinger equation

$$\hat{H} \psi(x) = E \psi(x)$$

Wavefunction

$$\Psi(x, t) = \psi(x) \cdot e^{-iEt/\hbar}$$

We have learned that the wavefunction

- gives a full description of the system
- physical observables can be extracted from the wavefunction
- is *not* a physical observable itself
- the probability distribution of finding the particle within volume element dV is given by $|\psi(r)|^2 dV$, postulated by Born

Not any given wavefunction is a good wavefunction. Born's interpretation of the wavefunction imposes some constraints onto what is an acceptable wavefunction. Second, because the wavefunction is a solution of the Schrödinger equation, which is a second order differential equation, there are further constraints on what is an acceptable wavefunction.

1. The square modulus of the wavefunction must be single valued in order to fulfill Born's postulate that $|\psi(r)|^2$ is the probability density.

Because the probability of finding a particle at dV can only be one value, it follows that $|\psi(r)|^2$ and thus $\psi(r)$ must be single valued.

2. The wavefunction must not be infinite over a finite region. If it were, it would violate Born's postulate in the sense that the probability of finding the particle somewhere must be a finite number. The wavefunction can be come infinite only over an infinitesimal region, because then the integral can still yield a finite value. The delta function is a good example of such a case:

$$\int \delta(x - a) dx = 1$$

3. The wavefunction must be continuous everywhere. Discontinuous wavefunctions have ill-behaved second order derivatives, which violates the fact that the wavefunction needs to be a solution of a second order differential equation.
4. The wavefunction must have a continuous first order derivative. No sudden kinks are allowed. This does not hold in regions of ill-behaved potential energy

Angular Momentum

In three dimensions, we can think of the angular momentum as a vector with a magnitude and projections onto the x , y and z axes. Both the magnitude and the projections are quantized. The magnitude of the angular momentum depends solely on l and is given by:

$$\{l(l+1)\}^{1/2} \hbar$$

Its projection on the z -axis is labeled by m_l . The magnitude for the z -component of the angular momentum can be found by operating with the \hat{l}_z operator onto the spherical harmonics.

$$\hat{l}_z Y_{l,m_l} = \hat{l}_z \Theta_{l,m_l} \Phi_{m_l} = \Theta_{l,m_l} \hat{l}_z \Phi_{m_l} = m_l \hbar \Theta_{l,m_l} \Phi_{m_l} = m_l \hbar Y_{l,m_l}$$

The projection of the angular momentum onto the z -axis thus takes on the values $m_l \hbar$. It is restricted to only $2l+1$ values for a given l . When the projection on the z -axis is well-determined, we lose information on the x and y -components of the angular momentum. This is a consequence of the fact that the \hat{l}_z does not commute with \hat{l}_x or \hat{l}_y , as we will see in the next chapter.

The Radial Schrödinger Equation

The Coulombic potential energy is:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

The full Hamiltonian of the electron-nucleus system is therefore:

$$\hat{H} = -\frac{\hbar^2}{2m_n}\nabla_{r_n}^2 - \frac{\hbar^2}{2m_e}\nabla_{r_e}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

In order to solve the Schrödinger equation using this Hamiltonian, we need to consider the following points:

1. Separating the degrees of freedom of the electron from those of the nucleus, so that we are only dealing with electronic wavefunctions.
2. Separating the angular motion from the motion in the radial direction. The Coulombic potential only depends on r and is independent of (θ, ϕ) . This suggests that we might be able to solve the problem considering only the radial coordinate.

The first point is readily achieved by writing the Hamiltonian in terms of the center-of-mass coordinates and the relative distance between the nucleus and the electron. For the kinetic energy part it is found that:

$$\begin{aligned} M &= m_n + m_e, & \frac{1}{\mu} &= \frac{1}{m_n} + \frac{1}{m_e} \\ R &= \frac{m_e r_e + m_n r_n}{M}, & r &= r_n - r_e \\ -\frac{\hbar^2}{2m_n}\nabla_{r_n}^2 - \frac{\hbar^2}{2m_e}\nabla_{r_e}^2 &= -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 \end{aligned}$$

The potential energy contribution is only dependent on relative distance r . We then only solve for the relative distance and ignore the overall translational

motion of the atom in space, in which case the Schrödinger equation becomes:

$$\begin{aligned} -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi &= E\psi \\ \frac{1}{r}\frac{d^2}{dr^2}r\psi + \frac{1}{r^2}\Lambda^2\psi + \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r}\psi &= -\left(\frac{2\mu E}{\hbar^2}\right)\psi \end{aligned}$$

To achieve the second point, we will write the wavefunction as $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, where $Y(\theta, \phi)$ are the spherical harmonics that are the solutions in the angular dimension. If we substitute these functions into the Schrödinger equation we get:

$$\begin{aligned} \frac{1}{r}\frac{d^2}{dr^2}rRY - \frac{l(l+1)}{r^2}RY + \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r}RY &= -\left(\frac{2\mu E}{\hbar^2}\right)RY \\ \frac{1}{r}\frac{d^2(rR)}{dr^2} + \left\{\frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r} - \frac{l(l+1)}{r^2}\right\}R &= -\left(\frac{2\mu E}{\hbar^2}\right)R \end{aligned}$$

We first multiply this equation with r , and then define the function $\Pi = rR$. We then can write the Schrödinger equation, which depends only on the radial coordinate r , as:

$$\frac{d^2\Pi}{dr^2} - \left(\frac{2\mu}{\hbar^2}\right)V_{eff}\Pi = -\left(\frac{2\mu E}{\hbar^2}\right)\Pi$$

where the effective potential is defined as:

$$V_{eff} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Note the following:

- The angular part has been divided out in the Schrödinger equation. The contribution from the angular dimension is implicitly present in the effective potential through the $l(l+1)\hbar^2$ term.
- The coulombic part provides an attractive (negative) potential. The angular term, however, provides a repulsive (positive) potential. These two effects will counterbalance depending on the quantum number l and the distance from the nucleus r .
- The angular centrifugal force is zero for $l = 0$. This implies that the potential is purely attractive and thus that there is a finite chance of finding the electron at the nucleus.
- Close to the nucleus, the angular centrifugal force for $l \neq 0$ is larger than the attractive coulombic force. Consequently, the electron is expelled from the nucleus and the probability of finding the electron at the nucleus is zero.

Angular Momentum Operators

The angular momentum and its operators play a central role in quantum mechanics. The reason for this is that with the set of angular momentum operator properties we can investigate quantum mechanical systems very thoroughly without turning to the Schrödinger equation, the explicit form of the wavefunctions or even the explicit form of the operators. All we shall use are the operators and their commutation relations, and with it we will be able to draw important conclusions about the corresponding observables.

The Fundamental Postulates of Quantum Mechanics

Quantum Mechanics can be formulated in terms of a few postulates (i.e., theoretical principles based on experimental observations). The goal of this section is to introduce such principles, together with some mathematical concepts that are necessary for that purpose. To keep the notation as simple as possible, expressions are written for a 1-dimensional system. The generalization to many dimensions is usually straightforward.

Postulate 1: Any system in a pure state can be described by a wave-function, $\psi(t, x)$, where t is a parameter representing the time and x represents the coordinates of the system. Such a function $\psi(t, x)$ must be continuous, single valued and square integrable.

Note 1: As a consequence of Postulate 4, we will see that $P(t, x) = \psi^*(t, x)\psi(t, x)dx$ represents the probability of finding the system between x and $x + dx$ at time t .

Postulate 2: Any observable (i.e., any measurable property of the system) can be described by an operator. The operator must be linear and hermitian.

What is an operator

Definition 1: An operator \hat{O} is a mathematical entity that transforms a function $f(x)$ into another function $g(x)$ as follows, **R4(96)**

$$\hat{O}f(x) = g(x),$$

where f and g are functions of x .

What is a linear operator

Definition 3: An operator \hat{O} is linear if and only if (iff),

$$\hat{O}(af(x) + bg(x)) = a\hat{O}f(x) + b\hat{O}g(x),$$

where a and b are constants.

What is a Hermitian operator

Definition 4: An operator O is hermitian iff,

$$\int dx \phi_n^*(x) \hat{O} \psi_m(x) = \left[\int dx \psi_m^*(x) \hat{O} \phi_n(x) \right]^*,$$

where the asterisk represents the complex conjugate.

What is an eigen function. What is an eigen value

Definition 5: A function $\phi_n(x)$ is an eigenfunction of O iff,

$$\hat{O} \phi_n(x) = O_n \phi_n(x),$$

where O_n is a number called eigenvalue.

Property 1: The eigenvalues of a hermitian operator are real.

Proof: Using Definition 4, we obtain

$$\int dx \phi_n^*(x) \hat{O} \phi_n(x) - \left[\int dx \phi_n^*(x) \hat{O} \phi_n(x) \right]^* = 0,$$

therefore,

$$[O_n - O_n^*] \int dx \phi_n^*(x) \phi_n(x) = 0.$$

Since $\phi_n(x)$ are square integrable functions, then,

$$O_n = O_n^*.$$

Property 2: Different eigenfunctions of a hermitian operator (i.e., eigenfunctions with different eigenvalues) are orthogonal (i.e., the scalar product of two different eigenfunctions is equal to zero). Mathematically, if $\hat{O} \phi_n = O_n \phi_n$, and $\hat{O} \phi_m = O_m \phi_m$, with $O_n \neq O_m$, then $\int dx \phi_n^* \phi_m = 0$.

Proof:

$$\int dx \phi_m^* \hat{O} \phi_n - \left[\int dx \phi_n^* \hat{O} \phi_m \right]^* = 0,$$

and

$$[O_n - O_m] \int dx \phi_m^* \phi_n = 0.$$

Postulate 3: The only possible experimental results of a measurement of an observable are the eigenvalues of the operator that corresponds to such observable.

Postulate 4: The average value of many measurements of an observable O , when the system is described by $\psi(x)$ as equal to the expectation value \bar{O} , which is defined as follows,

$$\bar{O} = \frac{\int dx \psi(x)^* \hat{O} \psi(x)}{\int dx \psi(x)^* \psi(x)}.$$

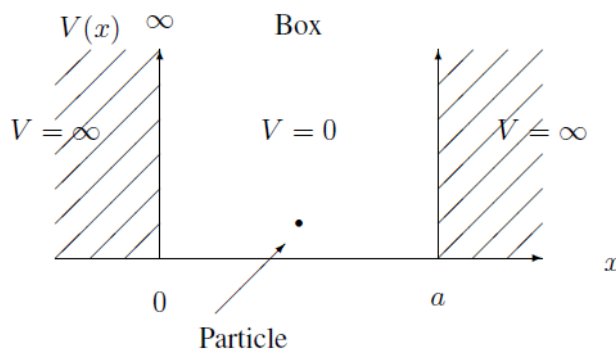
Postulate 5: The evolution of $\psi(x, t)$ in time is described by the time-dependent Schrödinger equation:

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = \hat{H} \psi(x, t),$$

where $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x)$, is the operator associated with the total energy of the system, $E = \frac{p^2}{2m} + V(x)$.

Particle in a box

The particle in the box can be represented by the following diagram: **R1(22)**



The goal of this section is to show that a particle with energy E and mass m in the box-potential $V(x)$ defined as

$$V(x) = \begin{cases} 0, & \text{when } 0 \leq x \leq a, \\ \infty, & \text{otherwise,} \end{cases}$$

has *stationary states* and a *discrete absorption spectrum* (i.e., the particle absorbs only certain discrete values of energy called *quanta*). To that end, we first solve the equation $\hat{H}\tilde{\phi}(x) = E\tilde{\phi}(x)$, and then we obtain the stationary states $\psi(x, t) = \tilde{\phi}(x)\exp(-\frac{i}{\hbar}Et)$.

Since $\tilde{\phi}(x)$ has to be continuous, single valued and square integrable (see Postulate 1), $\tilde{\phi}(0)$ and $\tilde{\phi}(a)$ must satisfy the appropriate boundary conditions both inside and outside the box. The boundary conditions inside the box lead to:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Phi(x) = E\Phi(x), \quad \Rightarrow \quad \Phi(x) = A \sin(Kx). \quad (6)$$

Functions $\Phi(x)$ determine the stationary states inside the box. The boundary conditions outside the box are,

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Phi(x) + \infty \Phi(x) = E\Phi(x), \quad \Rightarrow \quad \Phi(x) = 0,$$

and determine the energy associated with $\Phi(x)$ inside the box as follows. From Eq. (6), we obtain:

$$\frac{\hbar^2}{2m}AK^2 = EA, \quad \text{and,} \quad \Phi(a) = A\sin(Ka) = 0,$$

$$\Rightarrow Ka = n\pi, \quad \text{with } n = 1, 2, \dots \Rightarrow$$

Note that the number of *nodes* of Φ (i.e., the number of coordinates where $\Phi(x) = 0$), is equal to $n - 1$ for a given energy, and the energy levels are,

$$E = \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{a^2}, \quad \text{with } n = 1, 2, \dots$$

e.g.,

$$E(n=1) = \frac{\hbar^2}{2m} \frac{\pi^2}{a^2},$$

$$E(n=2) = \frac{\hbar^2}{2m} \frac{4\pi^2}{a^2}, \dots$$

Conclusion: The energy of the particle in the box is quantized! (i.e., the absorption spectrum of the particle in the box is not continuous but discrete).

Commutator

The *commutator* $[\hat{A}, \hat{B}]$ is defined as follows: **R4(97)**

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}.$$

Two operators \hat{A} and \hat{B} are said to *commute* when $[\hat{A}, \hat{B}] = 0$.

Schrodinger equation

Postulate 1.1 *The quantum state of the system is a solution of the Schrödinger equation*

$$i\hbar\partial_t|\psi(t)\rangle = H|\psi(t)\rangle, \quad (1.20)$$

where H is the quantum mechanical analogue of the classical Hamiltonian.

From classical mechanics, H is the sum of the kinetic and potential energy of a particle,

$$H = \frac{1}{2m}p^2 + V(x). \quad (1.21)$$

Thus, using the quantum analogues of the classical x and p , the quantum H is

$$H = \frac{1}{2m}\hat{p}^2 + V(\hat{x}). \quad (1.22)$$

To evaluate $V(\hat{x})$ we need a theorem that a function of an operator is the function evaluated at the eigenvalue of the operator. The proof is straight forward, Taylor expand the function about some point, If

$$V(x) = (V(0) + xV'(0) + \frac{1}{2}V''(0)x^2 \dots) \quad (1.23)$$

then

$$V(\hat{x}) = (V(0) + \hat{x}V'(0) + \frac{1}{2}V''(0)\hat{x}^2 \dots) \quad (1.24)$$

Since for any operator

$$[\hat{f}, \hat{f}^p] = 0 \forall p \quad (1.25)$$

Thus, we have

$$\langle x|V(\hat{x})|\psi\rangle = V(x)\psi(x) \quad (1.26)$$

So, in coordinate form, the Schrödinger Equation is written as

$$i\hbar \frac{\partial}{\partial t}\psi(x, t) = \left(-\frac{\hbar}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x, t) \quad (1.27)$$

Product of operators

An operator product is defined as

$$(\hat{A}\hat{B})|\psi\rangle = \hat{A}[\hat{B}|\psi\rangle] \quad (2.109)$$

where we operate in order from right to left. We proved that in general the ordering of the operations is important. In other words, we cannot in general write $\hat{A}\hat{B} = \hat{B}\hat{A}$. An example of this is the position and momentum operators. We have also defined the “commutator”

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (2.110)$$

Let's now briefly go over how to perform algebraic manipulations using operators and commutators. These are straightforward to prove

Textbook

1. A.K.Chandra, 2010, Introductory quantum Chemistry, Tata McGraw Hill Education Pvt., Ltd, New Delhi
2. Puri Sharma and Pathania, 2013, Elements of Physical Chemistry, Vishal Publishing Co., New Delhi

Possible Questions

PART- A Questions

(Each question carries one mark)

1. Evidence in favour of the wave nature of radiation
 - a. **Interference of radiation**
 - b. Photoelectric effect
 - c. Compton effect
 - d. Black body radiation

2. Black body radiation has a characteristic
 - a. **Continuous spectrum**
 - b. Discontinuous spectrum
 - c. Narrow range of light
 - d. Laser action
3. As per Planck's law the characteristic continuous spectrum of radiation depends upon
 - a. **Body's temperature**
 - b. Nature of the body
 - c. Colour of the body
 - d. Density of the body
4. Stefan Boltzmann law is based on
 - a. Diffraction of radiation
 - b. Photoelectric effect
 - c. Compton effect
 - d. **Black body radiation**
5. In one dimensional box problem the potential energy of the particle inside the box is
 - a. **zero**
 - b. unity
 - c. infinity
 - d. fractional
6. The solution of the problem of the rigid rotator gives us directly the solution of the
 - a. **angular momentum operator**
 - b. Laplacian operator
 - c. Hermitian operator
 - d. Position operator
7. A diatomic vibrating molecule can be represented by a simple model called
 - a. **Simple harmonic oscillator**
 - b. Rigid rotor
 - c. Particle in one dimensional box
 - d. Particle in three dimensional box
8. The quantum number 'n' is called
 - a. **Principal quantum number**
 - b. Azimuthal quantum number
 - c. Magnetic quantum number
 - d. Angular momentum quantum number
9. The lowest energy orbital for the ammonia molecule is designated
 - a. 1s
 - b. $1\sigma_g$
 - c. **$1a_1$**
 - d. C_{3v}
10. The benzene molecule C_6H_6 has how many vibrational modes
 - a. 6
 - b. 12
 - c. 24
 - d. **30**
11. Zeeman effect is
 - a. **the change in energy levels of an atom when it is placed in uniform external field**
 - b. The change in energy levels of an atom when placed in non-uniform external field
 - c. The change in energy levels of an atom when placed in external electric field
 - d. The change in energy levels of an atom when placed in non-uniform electric field
12. The energy level belongs to $E_n = 2n - 1/2$
 - a. **Harmonic oscillator**
 - b. Hydrogen atom
 - c. particle in a box
 - d. free particle in motion
13. For the symmetry operation "reflection" the corresponding symmetry element is
 - a. Identity element
 - b. **Plane of symmetry**
 - c. Centre of symmetry
 - d. Proper axis of symmetry
14. An array of numbers arranged in rows and columns are called
 - a. **Matrices**
 - b. determinants
 - c. Space lattices
 - d. Miller indices
15. A diagonal matrix will have
 - a. **In a square matrix if all the elements other than those along the diagonal are zero**
 - b. In a square matrix if all the elements other than those along the diagonal are unity
 - c. In a square matrix if all the elements along the diagonal are unity
 - d. In a square matrix if all the elements along the diagonal are zero
16. The molecule with C_{3v} point group
 - a. acetylene
 - b. water
 - c. **ammonia**
 - d. Boron trichloride
17. For a pyramidal molecule with point group C_{3v} the number of theoretically predicted IR fundamental bands

- a. **Three** b. Four c. Five d. Six
18. For chloro trifluoride molecule the number of observed Raman bands and IR bands are four each, the predicted geometry is
a. Pyramidal b. planar c. **T-shaped** d. bent
19. In case of molecules with a centre of symmetry the vibrational modes are anti-symmetric to centre of inversion are
a. IR inactive b. **IR active** c. Raman inactive d. Raman hyper active
20. For Raman activity the vibrations should involve a change in
a. **polarizability** b. magnetization
c. Magnetic susceptibility d. Surface tension

PART- B Questions

(Each question carries Six mark)

21. (a) Explain the different postulates of Quantum mechanics.
(OR)
(b) Explain Heisenberg's uncertainty principle .How it is experimentally verified?
22. (a) Set up Schrodinger wave equation for one dimensional harmonic oscillator and solve the equation for its energy and wave equation.
(OR)
(b) Derive the Schrodinger equation for rigid rotor.
23. (a) Explain the applications of variation method.
(OR)
(b) (i) Apply the perturbation method to helium atom.
(ii) Write a note on orbital and orbital shapes.
24. (a) Explain the different types of matrices with suitable examples.
(OR)
(b) Explain the following
(i) Square matrix (ii) diagonal matrix (iii) null matrix (iv) unit matrix
(v) Symmetric matrix
25. a. State and explain the great orthogonality theorem.
(OR)
b. Construct the character table C_{2v} group.

PART- C Question

(Each Question carries Ten mark)

26. (i) What are the relationships between reducible and irreducible representation of the group.
(ii) What are the Properties of irreducible representation?



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(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2017 & onwards)
Quantum Chemistry

Multiple Choice Questions for Unit I

S. No	Question	Option 1	Option 2	Option 3	Option 4	Answer
	Unit-I					
1	The definite region in three dimensional space around the nucleus where there is high probability of finding an electron of a specific energy E is called	Atomic orbital	Molecular orbital	Nodal plane	Median lobes	Atomic orbital
2	This involves with the knowledge of probability	Quantum mechanics	Classical mechanics	Newtonian mechanics	Fluid mechanics	Quantum mechanics
3	The knowledge of quantum mechanics usually involves a knowledge of	Probability	certainties	uncertainties	possibility	Probability
4	Classical mechanics and quantum mechanics tend to give the same results when systems are in highly excited quantum states. This is	Correspondence principle	Bohrs theory	Rutherford theory	Paulis exclusion principle	Correspondence principle
5	Classical mechanics and quantum mechanics tend to give the same results when systems are in	Normal states	Highly excited quantum states	Excited to low levels	When there is no excitation	Highly excited quantum states
6	In quantum mechanics the state of a system is defined by	Wave function	P,V, T	Gaseous laws	Law of mass action	Wave function

7	Simultaneous specification of position and momentum is impossible for a microscopic particle. This is	Stefan Boltzmann law	Weins displacement law	Planck's law	Heisenberg uncertainty principle	Heisenberg uncertainty principle
8	According to Newton's second law of motion	$F = ma$	$V = ma$	$F = mv$	$F = Pv$	$F = ma$
9	Which one of the following is correct in respect of an electron and a proton having same de-Broglie wavelength of 2 \AA	Both have same KE	The KE of proton is more than that of electron	Both have same velocity	Both have same momentum	Both have same momentum
10	The time independent Schrodinger's equation of a system represents the conservation of the	total binding energy of the system	total potential energy of the system	total kinetic energy of the system	total energy of the system	total energy of the system
11	According to Schrodinger, a particle is equivalent to a	wave packet	single wave	light wave	magnetic wave	wave packet
12	Matter waves are	longitudinal	electromagnetic	always travel with the speed of light	show diffraction	show diffraction
13	The de-broglie hypothesis is associated with	wave nature of electron only	wave nature of proton only	wave nature of radiation	wave nature of all material particles	wave nature of all material particles
14	The de-broglie wavelength of a charge q and accelerate through a potential difference of V volts is	$\lambda = h/\sqrt{mqV}$	$\lambda = h/m\sqrt{qV}$	$\lambda = h/\sqrt{2mqV}$	$\lambda = h/mqV$	$\lambda = h/\sqrt{2mqV}$
15	The de-broglie wavelength of a particle having KE E_K is given by	$\lambda = h/(\sqrt{E_K})$	$\lambda = h/(\sqrt{2mE_K})$	$\lambda = h/(\sqrt{mE_K})$	$\lambda = h/(\sqrt{3mE_K})$	$\lambda = h/(\sqrt{2mE_K})$
16	The value of Kronecker's delta, is equal to one when	$i = j$	i is not equal to j	$1/j = 2$	$i/j = 0$	$i = j$

17	The value of Kroneckers delta, is zero when	$i = j$	i is not equal to j	$1/j = 2$	$i/j = 0$	i is not equal to j
18	The component of linear momentum about any axis forms a	Discrete eigenspectrum	Continuous eigen spectrum	Continuous spectrum	Line spectrum	Continuous eigen spectrum
19	The component of angular momentum about any axis forms a	Discrete eigenspectrum	Continuous eigen spectrum	Continuous spectrum	Line spectrum	Discrete eigenspectrum
20	Momentum of a particle is	Mass x velocity	Mass / velocity	Mass x velocity x velocity	M^2/v	Mass x velocity
21	The eigen values for energy must be	real	imaginary	Complex number	positive	real
22	The eigen values for augular momentum must be	real	imaginary	Complex number	positive	real
23	Hermitian operator is	Linear and has real eigen values	Non linear and real eigen values	Linear and has imaginary eigen values	Non linear and imaginary eigen values	Linear and has real eigen values
24	The eigen values for observable physical quantities must be	real	imaginary	Complex number	positive	real
25	In using operators commutator means	Multiplying by zero	Adding 1	Dividing by 2	Multiplying by 2	Multiplying by zero
26	The operators d/dx and multiplication by x	Do not commute	commute	Is not a linear function	Results in a non-linear function	Do not commute
27	The classical expression for the total energy of a single particle of mass m is	Hamiltonian	hermitian	Laplacian	Eigen function	Hamiltonian

28	If in operating on the sum of two functions an operator gives the same result as the sum of the operations on the two functions separately	Linear operator	Addition operator	Subtracting operator	Vector operator	Linear
29	If the results of two operations is same regardless of the sequence in which the operations are performed, the two operators are said to	Commutate	associate	Get squared	multiplied	commute
30	If the same operator is applied several times in succession it is written with a	power	+ve sign	-ve sign	Division sign	power
31	The consecutive operations with two or more operators on a function is called as	Multiplication operator	Addition operator	Subtracting operator	Vector operator	Multiplication operator
32	If the operator is integration with respect to x on the operand x^3 , then the result of the operation is	$X^4/4 + C$	$X^{3/2}$	Kx^3	$3x^2$	$X^4/4 + C$
33	If the operator is differentiating with respect to x on the operand x^3 , then the result of the operation is	X^6	$X^{3/2}$	Kx^3	$3x^2$	$3x^2$
34	If the operator is multiplying by a constant on the operand x^3 , then the result of the operation is	X^6	$X^{3/2}$	Kx^3	$3x^2$	Kx^3
35	If the operator is taking the square root on the operand x^3 , then the result of the operation is	X^6	$X^{3/2}$	Kx^3	$3x^2$	$X^{3/2}$
36	If the operator is taking the square on the operand x^3 , then the result of the operation is	X^6	$X^{3/2}$	Kx^3	$3x^2$	X^6

37	For the operator differentiation with respect to x , the operator is	d/dx	dx	fdx	udv	d/dx
38	A function on which the operation by a operator is carried out is	Operand	derivative	Physical variable	Chemical variable	Operand
39	An operator is a symbol for a certain mathematical procedures which transforms	One function to another function	One property to another	One eigen value to another value	One eigen function to another function	One function to another function
40	According to Born interpretation the result of the wave function implies that the probability of finding the electron in region dx is	Same wherever dx is situated	Different in different places	May be or may not be equal	zero	Same wherever dx is situated
41	An acceptable well behaved wavefunction (Ψ) will be	contineous	Discontinuous first derivative	Do not vanish at infinity	Multiple valued	contineous
42	One of the properties of the acceptable wavefunction (Ψ)	Never increases to infinity	Discontinuous first derivative	Do not vanish at infinity	Multiple valued	Never increases to infinity
43	One of the properties of the acceptable wavefunction (Ψ)	Single valued	Discontinuous first derivative	Do not vanish at infinity	Multiple valued	Single valued
44	At constant frequency, the photoelectric current increases with increasing	Intensity of incident radiation	Kinetic energy of radiation	Quantum of radiation	Particles of radiation	Intensity of incident radiation
45	Increasing the intensity of incident radiation in photo electric effect is due to	Increase of KE of light	Increase the number of electrons emitted in unit time	Decreases KE	KE remains same	Increase the number of electrons emitted in unit time

46	A process where ejection of electrons take place by the action of light is called	Diffraction of radiation	Photoelectric effect	Compton effect	Black body radiation	Photoelectric effect
47	The spectrum of black-body radiation at any temperature is related to the spectrum at any other temperature	Stefan Boltzmann law	Weins displacement law	Planck's law	Jean's law	Weins displacement law
48	The power emitted per unit area of the surface of a black body is directly proportional to the fourth power of its absolute temperature, the law is	Stefan Boltzmann law	Weins displacement law	Planck's law	Jean's law	Stefan Boltzmann law
49	Stefan Boltzmann law is based on	Diffraction of radiation	Photoelectric effect	Compton effect	Black body radiation	Black body radiation
50	Weins displacement law is based on	Diffraction of radiation	Photoelectric effect	Compton effect	Black body radiation	Black body radiation
51	As the black body is heated the spectrum shift to	Higher frequency side	Lower frequency side	Becomes a narrower band	Becomes a broad band	Higher frequency side
52	Black body radiation has a characteristic continuous spectrum of radiation which depends upon the body temperature, this is called	Planck's law	Faradays law	Boltzmann law	Jeans law	Planck's law
53	As per plancks law the characteristic continuous spectrum of radiation depends upon	Body's temperature	Nature of the body	Colour of the body	Density of the body	Body's temperature
54	Black body radiation has a characteristic continuous spectrum of radiation which depends upon	Body's temperature	Nature of the body	Colour of the body	Density of the body	Body's temperature
55	Black body radiation has a characteristic	Continuous spectrum	Discontinuous spectrum	Narrow range of	Laser action	Continuous spectrum

				light		
56	Evidence in favour of the particle nature of radiation	Diffraction of radiation	Compton effect	polarisation	interference	Compton effect
57	Evidence in favour of the particle nature of radiation	Diffraction of radiation	Black body radiation	polarisation	interference	Photoelectric effect
58	Evidence in favour of the particle nature of radiation	Diffraction of radiation	Photoelectric effect	polarisation	interference	Photoelectric effect
59	Evidence in favour of the wave nature of radiation	Diffraction of radiation	Photoelectric effect	Compton effect	Black body radiation	Diffraction of radiation
60	Evidence in favour of the wave nature of radiation	Interference of radiation	Photoelectric effect	Compton effect	Black body radiation	Interference of radiation

UNIT – II
Wave Function ψ

Particle in a one-dimensional box - quantization of energy - normalization of wave function - orthogonality of the particle in a one-dimensional box wave functions. Illustration of the uncertainty principle and correspondence principle with reference to the particle in a one-dimensional box - particle in a three dimensional box - separation of variables.

Solving of Schrodinger equation for one-dimensional harmonic oscillator. Harmonic oscillator model of a diatomic molecule. Illustration of the uncertainty principle and correspondence principle with reference to harmonic oscillator.

Solving of Schrodinger equation for a rigid rotor. Rigid rotor model of a diatomic molecule.

1.5 Heisenberg uncertainty principle

Since a free particle is represented by the wave packet $\Psi(x, t)$, we may regard the uncertainty Δx in the position of the wave packet as the uncertainty in the position of the particle. Likewise, the uncertainty Δk in the wave number is related to the uncertainty Δp in the momentum of the particle by $\Delta k = \Delta p/\hbar$. The uncertainty relation (1.23) for the particle is, then

$$\Delta x \Delta p \geq \hbar \quad (1.44)$$

This relationship is known as the *Heisenberg uncertainty principle*.

The consequence of this principle is that at any instant of time the position

of the particle is defined only as a range Δx and the momentum of the particle is defined only as a range Δp . The product of these two ranges or ‘uncertainties’ is of order \hbar or larger. The exact value of the lower bound is dependent on how the uncertainties are defined. A precise definition of the uncertainties in position and momentum is given in Sections 2.3 and 3.10.

The Heisenberg uncertainty principle is a consequence of the stipulation that a quantum particle is a wave packet. The mathematical construction of a wave packet from plane waves of varying wave numbers dictates the relation (1.44). It is *not* the situation that while the position and the momentum of the particle are well-defined, they cannot be measured simultaneously to any desired degree of accuracy. The position and momentum are, in fact, not simultaneously precisely defined. The more precisely one is defined, the less precisely is the other, in accordance with equation (1.44). This situation is in contrast to classical-mechanical behavior, where both the position and the momentum can, in principle, be specified simultaneously as precisely as one wishes.

In quantum mechanics, if the momentum of a particle is precisely specified so that $p = p_0$ and $\Delta p = 0$, then the function $A(p)$ is

$$A(p) = \delta(p - p_0)$$

The wave packet (1.37) then becomes

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \delta(p - p_0) e^{i(px - Et)/\hbar} dp = \frac{1}{\sqrt{2\pi\hbar}} e^{i(p_0x - Et)/\hbar}$$

which is a plane wave with wave number p_0/\hbar and angular frequency E/\hbar . Such a plane wave has an infinite value for the uncertainty Δx . Likewise, if the position of a particle is precisely specified, the uncertainty in its momentum is infinite.

Another Heisenberg uncertainty relation exists for the energy E of a particle and the time t at which the particle has that value for the energy. The uncertainty $\Delta\omega$ in the angular frequency of the wave packet is related to the uncertainty ΔE in the energy of the particle by $\Delta\omega = \Delta E/\hbar$, so that the relation (1.25) when applied to a free particle becomes

$$\Delta E \Delta t \geq \hbar \quad (1.45)$$

Again, this relation arises from the representation of a particle by a wave packet and is a property of Fourier transforms.

The relation (1.45) may also be obtained from (1.44) as follows. The uncertainty ΔE is the spread of the kinetic energies in a wave packet. If Δp is small, then ΔE is related to Δp by

$$\Delta E = \Delta \left(\frac{p^2}{2m} \right) = \frac{p}{m} \Delta p \quad (1.46)$$

The time Δt for a wave packet to pass a given point equals the uncertainty in its position x divided by the group velocity v_g

$$\Delta t = \frac{\Delta x}{v_g} = \frac{\Delta x}{v} = \frac{m}{p} \Delta x \quad (1.47)$$

Combining equations (1.46) and (1.47), we see that $\Delta E \Delta t = \Delta x \Delta p$. Thus, the relation (1.45) follows from (1.44). The Heisenberg uncertainty relation (1.45) is treated more thoroughly in Section 3.10.

2.1 The Schrödinger equation

In the previous chapter we introduced the wave function to represent the motion of a particle moving in the absence of an external force. In this chapter we extend the concept of a wave function to make it apply to a particle acted upon by a non-vanishing force, i.e., a particle moving under the influence of a potential which depends on position. The force F acting on the particle is related to the potential or potential energy $V(x)$ by

$$F = -\frac{dV}{dx} \quad (2.1)$$

As in Chapter 1, we initially consider only motion in the x -direction. In Section 2.7, however, we extend the formalism to include three-dimensional motion.

In Chapter 1 we associated the wave packet

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} A(p) e^{i(px-Et)/\hbar} dp \quad (2.2)$$

with the motion in the x -direction of a free particle, where the weighting factor $A(p)$ is given by

$$A(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-i(px-Et)/\hbar} dx \quad (2.3)$$

This wave packet satisfies a partial differential equation, which will be used as the basis for the further development of a quantum theory. To find this differential equation, we first differentiate equation (2.2) twice with respect to the distance variable x to obtain

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{-1}{\sqrt{2\pi\hbar^5}} \int_{-\infty}^{\infty} p^2 A(p) e^{i(px-Et)/\hbar} dp \quad (2.4)$$

Differentiation of (2.2) with respect to the time t gives

$$\frac{\partial \Psi}{\partial t} = \frac{-i}{\sqrt{2\pi\hbar^3}} \int_{-\infty}^{\infty} EA(p) e^{i(px-Et)/\hbar} dp \quad (2.5)$$

The total energy E for a free particle (i.e., for a particle moving in a region of constant potential energy V) is given by

$$E = \frac{p^2}{2m} + V$$

which may be combined with equations (2.4) and (2.5) to give

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

Schrödinger (1926) postulated that this differential equation is also valid when the potential energy is not constant, but is a function of position. In that case the partial differential equation becomes

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x)\Psi(x, t) \quad (2.6)$$

which is known as the *time-dependent Schrödinger equation*. The solutions $\Psi(x, t)$ of equation (2.6) are the *time-dependent wave functions*. An important goal in wave mechanics is solving equation (2.6) for $\Psi(x, t)$ using various expressions for $V(x)$ that relate to specific physical systems.

When $V(x)$ is not constant, the solutions $\Psi(x, t)$ to equation (2.6) may still be expanded in the form of a wave packet,

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} A(p, t) e^{i(px-Et)/\hbar} dp \quad (2.7)$$

The Fourier transform $A(p, t)$ is then, in general, a function of both p and time t , and is given by

$$A(p, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-i(px-Et)/\hbar} dx \quad (2.8)$$

By way of contrast, recall that in treating the free particle as a wave packet in Chapter 1, we required that the weighting factor $A(p)$ be independent of time and we needed to specify a functional form for $A(p)$ in order to study some of the properties of the wave packet.

2.2 The wave function

Interpretation

Before discussing the methods for solving the Schrödinger equation for specific choices of $V(x)$, we consider the meaning of the wave function. Since the wave function $\Psi(x, t)$ is identified with a particle, we need to establish the connection between $\Psi(x, t)$ and the observable properties of the particle. As in the

case of the free particle discussed in Chapter 1, we follow the formulation of Born (1926).

The fundamental postulate relating the wave function $\Psi(x, t)$ to the properties of the associated particle is that the quantity $|\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t)$ gives the *probability density* for finding the particle at point x at time t . Thus, the probability of finding the particle between x and $x + dx$ at time t is $|\Psi(x, t)|^2 dx$. The location of a particle, at least within an arbitrarily small interval, can be determined through a physical measurement. If a series of measurements are made on a number of particles, each of which has the exact same wave function, then these particles will be found in many different locations. Thus, the wave function does not indicate the actual location at which the particle will be found, but rather provides the probability for finding the particle in any given interval. More generally, quantum theory provides the probabilities for the various possible results of an observation rather than a precise prediction of the result. This feature of quantum theory is in sharp contrast to the predictive character of classical mechanics.

According to Born's statistical interpretation, the wave function completely describes the physical system it represents. There is no information about the system that is not contained in $\Psi(x, t)$. Thus, the *state* of the system is determined by its wave function. For this reason the wave function is also called the *state function* and is sometimes referred to as the state $\Psi(x, t)$.

The product of a function and its complex conjugate is always real and is positive everywhere. Accordingly, the wave function itself may be a real or a complex function. At any point x or at any time t , the wave function may be positive or negative. In order that $|\Psi(x, t)|^2$ represents a unique probability density for every point in space and at all times, the wave function must be continuous, single-valued, and finite. Since $\Psi(x, t)$ satisfies a differential equation that is second-order in x , its first derivative is also continuous. The wave function may be multiplied by a phase factor $e^{i\alpha}$, where α is real, without changing its physical significance since

$$[e^{i\alpha}\Psi(x, t)]^*[e^{i\alpha}\Psi(x, t)] = \Psi^*(x, t)\Psi(x, t) = |\Psi(x, t)|^2$$

Normalization

The particle that is represented by the wave function must be found with probability equal to unity somewhere in the range $-\infty \leq x \leq \infty$, so that $\Psi(x, t)$ must obey the relation

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 dx = 1 \quad (2.9)$$

A function that obeys this equation is said to be *normalized*. If a function $\Phi(x, t)$ is not normalized, but satisfies the relation

$$\int_{-\infty}^{\infty} \Phi^*(x, t)\Phi(x, t) dx = N$$

then the function $\Psi(x, t)$ defined by

$$\Psi(x, t) = \frac{1}{\sqrt{N}} \Phi(x, t)$$

is normalized.

In order for $\Psi(x, t)$ to satisfy equation (2.9), the wave function must be square-integrable (also called quadratically integrable). Therefore, $\Psi(x, t)$ must go to zero faster than $1/\sqrt{|x|}$ as x approaches (\pm) infinity. Likewise, the derivative $\partial\Psi/\partial x$ must also go to zero as x approaches (\pm) infinity.

Once a wave function $\Psi(x, t)$ has been normalized, it remains normalized as time progresses. To prove this assertion, we consider the integral

$$N = \int_{-\infty}^{\infty} \Psi^* \Psi dx$$

and show that N is independent of time for every function Ψ that obeys the Schrödinger equation (2.6). The time derivative of N is

$$\frac{dN}{dt} = \int_{-\infty}^{\infty} \frac{\partial}{\partial t} |\Psi(x, t)|^2 dx \quad (2.10)$$

where the order of differentiation and integration has been interchanged on the right-hand side. The derivative of the probability density may be expanded as follows

$$\frac{\partial}{\partial t} |\Psi(x, t)|^2 = \frac{\partial}{\partial t} (\Psi^* \Psi) = \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}$$

so that

$$\frac{\partial}{\partial t} |\Psi(x, t)|^2 = \frac{i\hbar}{2m} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) \quad (2.12)$$

Substitution of equation (2.12) into (2.10) and evaluation of the integral give

$$\frac{dN}{dt} = \frac{i\hbar}{2m} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) dx = \frac{i\hbar}{2m} \left[\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right]_{-\infty}^{\infty}$$

Since $\Psi(x, t)$ goes to zero as x goes to (\pm) infinity, the right-most term vanishes and we have

$$\frac{dN}{dt} = 0$$

Thus, the integral N is time-independent and the normalization of $\Psi(x, t)$ does not change with time.

Not all wave functions can be normalized. In such cases the quantity $|\Psi(x, t)|^2$ may be regarded as the *relative probability density*, so that the ratio

$$\frac{\int_{a_1}^{a_2} |\Psi(x, t)|^2 dx}{\int_{b_1}^{b_2} |\Psi(x, t)|^2 dx}$$

represents the probability that the particle will be found between a_1 and a_2 relative to the probability that it will be found between b_1 and b_2 . As an example, the plane wave

$$\Psi(x, t) = e^{i(px - Et)/\hbar}$$

does not approach zero as x approaches (\pm) infinity and consequently cannot be normalized. The probability density $|\Psi(x, t)|^2$ is unity everywhere, so that the particle is equally likely to be found in any region of a specified width.

Equation (2.6) and its complex conjugate may be written in the form

$$\begin{aligned}\frac{\partial \Psi}{\partial t} &= \frac{i\hbar}{2m} \frac{\partial^2 \Psi}{\partial x^2} - \frac{i}{\hbar} V \Psi \\ \frac{\partial \Psi^*}{\partial t} &= -\frac{i\hbar}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} + \frac{i}{\hbar} V \Psi^*\end{aligned}\quad (2.11)$$

so that $\partial |\Psi(x, t)|^2 / \partial t$ becomes

$$\frac{\partial}{\partial t} |\Psi(x, t)|^2 = \frac{i\hbar}{2m} \left(\Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^*}{\partial x^2} \right)$$

where the terms containing V cancel. We next note that

$$\frac{\partial}{\partial x} \left(\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right) = \Psi^* \frac{\partial^2 \Psi}{\partial x^2} - \Psi \frac{\partial^2 \Psi^*}{\partial x^2}$$

2.4 Time-independent Schrödinger equation

The first step in the solution of the partial differential equation (2.6) is to express the wave function $\Psi(x, t)$ as the product of two functions

$$\Psi(x, t) = \psi(x)\chi(t) \quad (2.27)$$

where $\psi(x)$ is a function of only the distance x and $\chi(t)$ is a function of only the time t . Substitution of equation (2.27) into (2.6) and division by the product $\psi(x)\chi(t)$ give

$$i\hbar \frac{1}{\chi(t)} \frac{d\chi(t)}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi(x)}{dx^2} + V(x) \quad (2.28)$$

The left-hand side of equation (2.28) is a function only of t , while the right-hand side is a function only of x . Since x and t are independent variables, each side of equation (2.28) must equal a constant. If this were not true, then the left-hand side could be changed by varying t while the right-hand side remained fixed and so the equality would no longer apply. For reasons that will soon be apparent, we designate this *separation constant* by E and assume that it is a real number.

Equation (2.28) is now separable into two independent differential equations, one for each of the two independent variables x and t . The time-dependent equation is

and is called the *time-independent Schrödinger equation*. The solution of this differential equation depends on the specification of the potential energy $V(x)$. Note that the separation of equation (2.6) into spatial and temporal parts is contingent on the potential $V(x)$ being time-independent.

The wave function $\Psi(x, t)$ is then

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \quad (2.31)$$

and the probability density $|\Psi(x, t)|^2$ is now given by

$$|\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t) = \psi^*(x)e^{iEt/\hbar}\psi(x)e^{-iEt/\hbar} = |\psi(x)|^2$$

Thus, the probability density depends only on the position variable x and does not change with time. For this reason the wave function $\Psi(x, t)$ in equation (2.31) is called a *stationary state*. If $\Psi(x, t)$ is normalized, then $\psi(x)$ is also normalized

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad (2.32)$$

which is the reason why we set the integration constant in equation (2.29) equal to unity.

The total energy, when expressed in terms of position and momentum, is called the *Hamiltonian*, H , and is given by

$$H(x, p) = \frac{p^2}{2m} + V(x)$$

The expectation value $\langle H \rangle$ of the Hamiltonian may be obtained by applying equation (2.22)

$$\langle H \rangle = \int_{-\infty}^{\infty} \Psi^*(x, t) \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \Psi(x, t) dx$$

For the stationary state (2.31), this expression becomes

$$\langle H \rangle = \int_{-\infty}^{\infty} \psi^*(x) \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) dx$$

If we substitute equation (2.30) into the integrand, we obtain

$$\langle H \rangle = E \int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx = E$$

where we have also applied equation (2.32). We have just shown that the separation constant E is the expectation value of the Hamiltonian, or the total energy for the stationary state, so that ' E ' is a desirable designation. Since the energy is a real physical quantity, the assumption that E is real is justified.

In the application of Schrödinger's equation (2.30) to specific physical examples, the requirements that $\psi(x)$ be continuous, single-valued, and square-integrable restrict the acceptable solutions to an infinite set of specific functions $\psi_n(x)$, $n = 1, 2, 3, \dots$, each with a corresponding energy value E_n . Thus, the energy is quantized, being restricted to certain values. This feature is illustrated in Section 2.5 with the example of a particle in a one-dimensional box.

Since the partial differential equation (2.6) is linear, any linear superposition of solutions is also a solution. Therefore, the most general solution of equation (2.6) for a time-independent potential energy $V(x)$ is

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar} \quad (2.33)$$

where the coefficients c_n are arbitrary complex constants. The wave function $\Psi(x, t)$ in equation (2.33) is not a stationary state, but rather a sum of stationary states, each with a different energy E_n .

2.5 Particle in a one-dimensional box

As an illustration of the application of the time-independent Schrödinger equation to a system with a specific form for $V(x)$, we consider a particle confined to a box with infinitely high sides. The potential energy for such a particle is given by

$$\begin{aligned} V(x) &= 0, & 0 \leq x \leq a \\ &= \infty, & x < 0, \quad x > a \end{aligned}$$

and is illustrated in Figure 2.1.

Outside the potential well, the Schrödinger equation (2.30) is given by

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \infty\psi = E\psi$$

for which the solution is simply $\psi(x) = 0$; the probability is zero for finding the particle outside the box where the potential is infinite. Inside the box, the Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

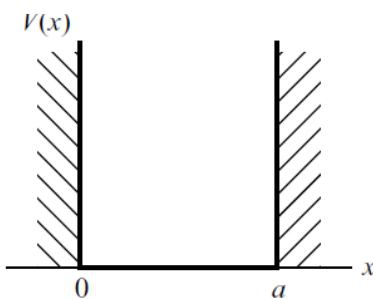


Figure 2.1 The potential energy $V(x)$ for a particle in a one-dimensional box of length a .

or

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \psi \quad (2.34)$$

where λ is the de Broglie wavelength,

$$\lambda = \frac{2\pi\hbar}{\sqrt{2mE}} = \frac{h}{p} \quad (2.35)$$

We have implicitly assumed here that E is not negative. If E were negative, then the wave function ψ and its second derivative would have the same sign. As $|x|$ increases, the wave function $\psi(x)$ and its curvature $d^2\psi/dx^2$ would become larger and larger in magnitude and $\psi(x)$ would approach (\pm) infinity as $x \rightarrow \infty$.

The solutions to equation (2.34) are functions that are proportional to their second derivatives, namely $\sin(2\pi x/\lambda)$ and $\cos(2\pi x/\lambda)$. The functions $\exp[2\pi i x/\lambda]$ and $\exp[-2\pi i x/\lambda]$, which as equation (A.31) shows are equivalent to the trigonometric functions, are also solutions, but are more difficult to use for this system. Thus, the general solution to equation (2.34) is

$$\psi(x) = A \sin \frac{2\pi x}{\lambda} + B \cos \frac{2\pi x}{\lambda} \quad (2.36)$$

where A and B are arbitrary constants of integration.

The constants A and B are determined by the *boundary conditions* placed on the solution $\psi(x)$. Since $\psi(x)$ must be continuous, the boundary conditions require that $\psi(x)$ vanish at each end of the box so as to match the value of $\psi(x)$ outside the box, i.e., $\psi(0) = \psi(a) = 0$. At $x = 0$, the function $\psi(0)$ from (2.36) is

$$\psi(0) = A \sin 0 + B \cos 0 = B$$

so that $B = 0$ and $\psi(x)$ is now

$$\psi(x) = A \sin \frac{2\pi x}{\lambda} \quad (2.37)$$

At $x = a$, $\psi(a)$ is

$$\psi(a) = A \sin \frac{2\pi a}{\lambda} = 0$$

The constant A cannot be zero, for then $\psi(x)$ would vanish everywhere and there would be no particle. Consequently, we have $\sin(2\pi a/\lambda) = 0$ or

$$\frac{2\pi a}{\lambda} = n\pi, \quad n = 1, 2, 3, \dots$$

where n is any positive integer greater than zero. The solution $n = 0$ would cause $\psi(x)$ to vanish everywhere and is therefore not acceptable. Negative values of n give redundant solutions because $\sin(-\theta)$ equals $-\sin \theta$.

We have found that only distinct values for the de Broglie wavelength satisfy the requirement that the wave function represents the motion of the particle. These distinct values are denoted as λ_n and are given by

$$\lambda_n = \frac{2a}{n}, \quad n = 1, 2, 3, \dots \quad (2.38)$$

Consequently, from equation (2.35) only distinct values E_n of the energy are allowed

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}, \quad n = 1, 2, 3, \dots \quad (2.39)$$

so that the energy for a particle in a box is quantized.

The lowest allowed energy level is called the *zero-point energy* and is given by $E_1 = h^2/8ma^2$. This zero-point energy is always greater than the zero value of the constant potential energy of the system and increases as the length a of

the box decreases. The non-zero value for the lowest energy level is related to the Heisenberg uncertainty principle. For the particle in a box, the uncertainty Δx in position is equal to the length a since the particle is somewhere within the box. The uncertainty Δp in momentum is equal to $2|p|$ since the momentum ranges from $-|p|$ to $|p|$. The momentum and energy are related by

$$|p| = \sqrt{2mE} = \frac{nh}{2a}$$

so that

$$\Delta x \Delta p = nh$$

is in agreement with the Heisenberg uncertainty principle (2.26). If the lowest allowed energy level were zero, then the Heisenberg uncertainty principle would be violated.

The allowed wave functions $\psi_n(x)$ for the particle in a box are obtained by substituting equation (2.38) into (2.37),

$$\psi_n(x) = A \sin \frac{n\pi x}{a}, \quad 0 \leq x \leq a$$

The remaining constant of integration A is determined by the normalization condition (2.32),

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = |A|^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = |A|^2 \frac{a}{\pi} \int_0^{\pi} \sin^2 n\theta d\theta = |A|^2 \frac{a}{2} = 1$$

where equation (A.15) was used. Therefore, we have

$$|A|^2 = \frac{2}{a}$$

or

$$A = e^{i\alpha} \sqrt{\frac{2}{a}}$$

Setting the phase α equal to zero since it has no physical significance, we obtain for the normalized wave functions

$$\begin{aligned} \psi_n(x) &= \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, & 0 \leq x \leq a \\ &= 0, & x < 0, \quad x > a \end{aligned} \quad (2.40)$$

The time-dependent Schrödinger equation (2.30) for the particle in a box has an infinite set of solutions $\psi_n(x)$ given by equation (2.40). The first four wave functions $\psi_n(x)$ for $n = 1, 2, 3$, and 4 and their corresponding probability densities $|\psi_n(x)|^2$ are shown in Figure 2.2. The wave function $\psi_1(x)$ corresponding to the lowest energy level E_1 is called the *ground state*. The other wave functions are called *excited states*.

If we integrate the product of two different wave functions $\psi_l(x)$ and $\psi_n(x)$, we find that

$$\int_0^a \psi_l(x) \psi_n(x) dx = \frac{2}{a} \int_0^a \sin\left(\frac{l\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) dx = \frac{2}{\pi} \int_0^\pi \sin l\theta \sin n\theta d\theta = 0 \quad (2.41)$$

where equation (A.15) has been introduced. This result may be combined with the normalization relation to give

$$\int_0^a \psi_l(x) \psi_n(x) dx = \delta_{ln} \quad (2.42)$$

where δ_{ln} is the Kronecker delta,

$$\begin{aligned} \delta_{ln} &= 1, & l &= n \\ &= 0, & l &\neq n \end{aligned} \quad (2.43)$$

Functions that obey equation (2.41) are called *orthogonal functions*. If the orthogonal functions are also normalized, as in equation (2.42), then they are

said to be *orthonormal*. The orthogonal property of wave functions in quantum mechanics is discussed in a more general context in Section 3.3.

The stationary states $\Psi(x, t)$ for the particle in a one-dimensional box are given by substitution of equations (2.39) and (2.40) into (2.31),

$$\Psi(x, t) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) e^{-i(n^2\pi^2\hbar/2ma^2)t} \quad (2.44)$$

The most general solution (2.33) is, then,

$$\Psi(x, t) = \sqrt{\frac{2}{a}} \sum_n c_n \sin\left(\frac{n\pi x}{a}\right) e^{-i(n^2\pi^2\hbar/2ma^2)t} \quad (2.45)$$

2.8 Particle in a three-dimensional box

A simple example of a three-dimensional system is a particle confined to a rectangular container with sides of lengths a , b , and c . Within the box there is no force acting on the particle, so that the potential $V(\mathbf{r})$ is given by

$$V(\mathbf{r}) = 0, \quad 0 \leq x \leq a, \quad 0 \leq y \leq b, \quad 0 \leq z \leq c$$

$$= \infty, \quad x < 0, \quad x > a; \quad y < 0, \quad y > b; \quad z < 0, \quad z > c$$

The wave function $\psi(\mathbf{r})$ outside the box vanishes because the potential is infinite there. Inside the box, the wave function obeys the Schrödinger equation (2.70) with the potential energy set equal to zero

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(\mathbf{r})}{\partial x^2} + \frac{\partial^2 \psi(\mathbf{r})}{\partial y^2} + \frac{\partial^2 \psi(\mathbf{r})}{\partial z^2} \right) = E\psi(\mathbf{r}) \quad (2.75)$$

The standard procedure for solving a partial differential equation of this type is to assume that the function $\psi(\mathbf{r})$ may be written as the product of three functions, one for each of the three variables

$$\psi(\mathbf{r}) = \psi(x, y, z) = X(x)Y(y)Z(z) \quad (2.76)$$

Thus, $X(x)$ is a function only of the variable x , $Y(y)$ only of y , and $Z(z)$ only of z . Substitution of equation (2.76) into (2.75) and division by the product XYZ give

$$\frac{-\hbar^2}{2mX} \frac{d^2 X}{dx^2} + \frac{-\hbar^2}{2mY} \frac{d^2 Y}{dy^2} + \frac{-\hbar^2}{2mZ} \frac{d^2 Z}{dz^2} = E \quad (2.77)$$

The first term on the left-hand side of equation (2.77) depends only on the variable x , the second only on y , and the third only on z . No matter what the values of x , or y , or z , the sum of these three terms is always equal to the same constant E . The only way that this condition can be met is for each of the three terms to equal some constant, say E_x , E_y , and E_z , respectively. The partial differential equation (2.77) can then be separated into three equations, one for each variable

$$\frac{d^2 X}{dx^2} + \frac{2m}{\hbar^2} E_x X = 0, \quad \frac{d^2 Y}{dy^2} + \frac{2m}{\hbar^2} E_y Y = 0, \quad \frac{d^2 Z}{dz^2} + \frac{2m}{\hbar^2} E_z Z = 0 \quad (2.78)$$

where

$$E_x + E_y + E_z = E \quad (2.79)$$

Thus, the three-dimensional problem has been reduced to three one-dimensional problems.

The differential equations (2.78) are identical in form to equation (2.34) and the boundary conditions are the same as before. Consequently, the solutions inside the box are given by equation (2.40) as

$$\begin{aligned} X(x) &= \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}, & n_x &= 1, 2, 3, \dots \\ Y(y) &= \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}, & n_y &= 1, 2, 3, \dots \\ Z(z) &= \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}, & n_z &= 1, 2, 3, \dots \end{aligned} \quad (2.80)$$

and the constants E_x , E_y , E_z are given by equation (2.39)

$$\begin{aligned} E_x &= \frac{n_x^2 h^2}{8ma^2}, & n_x &= 1, 2, 3, \dots \\ E_y &= \frac{n_y^2 h^2}{8mb^2}, & n_y &= 1, 2, 3, \dots \\ E_z &= \frac{n_z^2 h^2}{8mc^2}, & n_z &= 1, 2, 3, \dots \end{aligned} \quad (2.81)$$

The quantum numbers n_x , n_y , n_z take on positive integer values independently of each other. Combining equations (2.76) and (2.80) gives the wave functions inside the three-dimensional box

$$\psi_{n_x, n_y, n_z}(\mathbf{r}) = \sqrt{\frac{8}{v}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad (2.82)$$

where $v = abc$ is the volume of the box. The energy levels for the particle are obtained by substitution of equations (2.81) into (2.79)

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad (2.83)$$

Degeneracy of energy levels

If the box is cubic, we have $a = b = c$ and the energy levels become

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad (2.84)$$

The lowest or zero-point energy is $E_{1,1,1} = 3h^2/8ma^2$, which is three times the zero-point energy for a particle in a one-dimensional box of the same length. The second or next-highest value for the energy is obtained by setting one of

the integers n_x, n_y, n_z equal to 2 and the remaining ones equal to unity. Thus, there are three ways of obtaining the value $6h^2/8ma^2$, namely, $E_{2,1,1}$, $E_{1,2,1}$, and $E_{1,1,2}$. Each of these three possibilities corresponds to a different wave function, respectively, $\psi_{2,1,1}(\mathbf{r})$, $\psi_{1,2,1}(\mathbf{r})$, and $\psi_{1,1,2}(\mathbf{r})$. An energy level that corresponds to more than one wave function is said to be *degenerate*. The second energy level in this case is threefold or triply degenerate. The zero-point energy level is *non-degenerate*. The energies and degeneracies for the first six energy levels are listed in Table 2.1.

The degeneracies of the energy levels in this example are the result of symmetry in the lengths of the sides of the box. If, instead of the box being cubic, the lengths of b and c in terms of a were $b = a/2$, $c = a/3$, then the values of the energy levels and their degeneracies are different, as shown in Table 2.2 for the lowest eight levels.

Orthogonality theorem

If ψ_1 and ψ_2 are eigenfunctions of a hermitian operator \hat{A} with different eigenvalues α_1 and α_2 , then ψ_1 and ψ_2 are orthogonal. To prove this theorem, we begin with the integral

$$\langle \psi_2 | \hat{A} \psi_1 \rangle = \alpha_1 \langle \psi_2 | \psi_1 \rangle \quad (3.17)$$

Since \hat{A} is hermitian and α_2 is real, the left-hand side may be written as

$$\langle \psi_2 | \hat{A} \psi_1 \rangle = \langle \hat{A} \psi_2 | \psi_1 \rangle = \alpha_2 \langle \psi_2 | \psi_1 \rangle$$

Thus, equation (3.17) becomes

$$(\alpha_2 - \alpha_1) \langle \psi_2 | \psi_1 \rangle = 0$$

Since $\alpha_1 \neq \alpha_2$, the functions ψ_1 and ψ_2 are orthogonal.

Rigid Rotor

We can expand our analysis to a two-particle system with masses m_1 and m_2 that rotate with a fixed distance R between them. We can separate out the

translational motion of the system as a whole and their motion relative to one another. Instead of using the separate masses m_1 and m_2 , we can define the joint mass M and the reduced mass μ as follows:

$$\begin{aligned} M &= m_1 + m_2 \\ \frac{1}{\mu} &= \frac{1}{m_1} + \frac{1}{m_2} \end{aligned}$$

Using the technique of the separation of variables, the Schrödinger equation can be split into an equation that depends on the center coordinates and the joint mass M , and an equation that depends on the relative coordinates of the system with reduced mass μ :

$$\begin{aligned} -\frac{\hbar^2}{2M} \nabla_M^2 \Psi_M &= E_M \Psi_M \\ -\frac{\hbar^2}{2\mu} \nabla_\mu^2 \Psi_\mu &= E_\mu \Psi_\mu \end{aligned}$$

The total wavefunction is written as $\Psi = \Psi_M \Psi_\mu$ and the total energy is $E = E_M + E_\mu$. We are only concerned with the relative motion of the system. For constant r we then have for the Schrödinger equation:

$$-\frac{\hbar^2}{2I} \Lambda^2 \Psi_\mu = E \Psi_\mu$$

This is the same problem as the particle on a sphere. The solutions are the spherical harmonics and the energies are:

$$E = J(J+1) \frac{\hbar^2}{2I}$$

where the labels J and M_J are used for labeling the states of the rigid rotor.

The quantum behavior of the harmonic oscillator

This physical system serves as an excellent example for illustrating the basic principles of quantum mechanics. The Schroedinger equation for the harmonic oscillator can be solved rigorously and exactly for the energy eigenvalues and eigenstates. The mathematical process for the solution is neither trivial, as is the case for the particle in a box, nor excessively complicated. Moreover, we have the opportunity to introduce the ladder operator technique for solving the eigenvalue problem.

The harmonic oscillator is an important system in the study of physical phenomena in both classical and quantum mechanics. Classically, the harmonic oscillator describes the mechanical behavior of a spring and, by analogy, other phenomena such as the oscillations of charge flow in an electric circuit, the vibrations of sound-wave and light-wave generators, and oscillatory chemical reactions. The quantum-mechanical treatment of the harmonic oscillator may be applied to the vibrations of molecular bonds and has many other applications in quantum physics and field theory.

4.2 Quantum treatment

The classical Hamiltonian $H(x, p)$ for the harmonic oscillator is

$$H(x, p) = \frac{p^2}{2m} + V(x) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (4.11)$$

The Hamiltonian operator $\hat{H}(x, \hat{p})$ is obtained by replacing the momentum p in equation (4.11) with the momentum operator $\hat{p} = -i\hbar d/dx$

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \quad (4.12)$$

The Schrödinger equation is, then

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi(x) = E\psi(x) \quad (4.13)$$

It is convenient to introduce the dimensionless variable ξ by the definition

$$\xi = \left(\frac{m\omega}{\hbar}\right)^{1/2} x \quad (4.14)$$

so that the Hamiltonian operator becomes

$$\hat{H} = \frac{\hbar\omega}{2} \left(\xi^2 - \frac{d^2}{d\xi^2} \right) \quad (4.15)$$

Since the Hamiltonian operator is written in terms of the variable ξ rather than x , we should express the eigenstates in terms of ξ as well. Accordingly, we define the functions $\phi(\xi)$ by the relation

$$\phi(\xi) = \left(\frac{\hbar}{m\omega}\right)^{1/4} \psi(x) \quad (4.16)$$

If the functions $\psi(x)$ are normalized with respect to integration over x

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

then from equations (4.14) and (4.16) we see that the functions $\phi(\xi)$ are normalized with respect to integration over ξ

$$\int_{-\infty}^{\infty} |\phi(\xi)|^2 d\xi = 1$$

The Schrödinger equation (4.13) then takes the form

$$-\frac{d^2\phi(\xi)}{d\xi^2} + \xi^2\phi(\xi) = \frac{2E}{\hbar\omega}\phi(\xi) \quad (4.17)$$

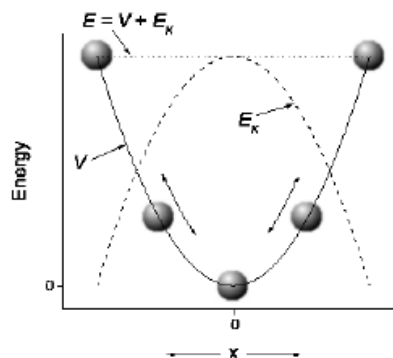
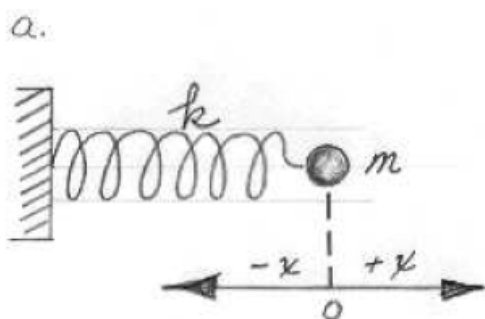
Since the Hamiltonian operator is hermitian, the energy eigenvalues E are real.

There are two procedures available for solving this differential equation. The older procedure is the Frobenius or series solution method. The solution of equation (4.17) by this method is presented in Appendix G. In this chapter we use the more modern ladder operator procedure. Both methods give exactly the same results.

The Harmonic Oscillator

The Classical Harmonic Oscillator

A vibrating body subject to a restoring force, which increases in proportion to the displacement from equilibrium, will undergo harmonic motion at constant frequency and is called a harmonic oscillator. Figure 1(a) shows one example of a harmonic oscillator, where a body of mass m is connected to a fixed support by a spring with a force constant, k . We will assume that gravitational forces are absent.



Harmonic Oscillator Consisting of a Mass Connected by a Spring to a Fixed Support;
(b) Potential Energy, V , and Kinetic Energy, E_K For the Harmonic Oscillator.

When the system is at equilibrium, the mass will be at rest, and at this point the displacement, x , from equilibrium has the value zero. As the mass is pulled to the right, there will be a restoring force, f , which is proportional to the displacement. For a spring obeying Hooke's law,

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

The minus sign in equation 1 is related to the fact that the force will be negative, since the mass will tend to be pulled toward the $-x$ direction when the force is positive. From Newton's second law, the force will be equal to the mass multiplied by the acceleration, $\frac{d^2x}{dt^2}$. The equation of motion is a second order ordinary differential equation, obtained by rearranging equation 1 as

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

and has a general solution given by

$$x(t) = A \sin \omega t + B \cos \omega t, \quad (3)$$

where

$$\omega = (k/m)^{1/2}. \quad (4)$$

The units of ω are radians s^{-1} , and since there are 2π radians/cycle, the frequency $\nu = \omega/2\pi$ cycles s^{-1} . [Note: The student should check this solution by substituting equation 3 back into equation 2].

We again require two boundary conditions to specify the constants A and B . We choose the mass to be at $x = 0$ moving with a velocity v_0 at time = 0. The first condition gives

$$x(t = 0) = A \cdot 0 + B \cdot 1 = B = 0 \quad (5)$$

so that

$$x(t) = A \sin \omega t. \quad (6)$$

Using this result, the second boundary condition can be written as

$$v_0 = v(t = 0) = \left. \frac{dx}{dt} \right|_{t=0} = A\omega \cos \omega t|_{t=0} = A\omega, \quad (7)$$

from which we see that $A = v_0/\omega$. As the spring stretches, or contracts, when the mass is undergoing harmonic motion, the potential energy of the system will rise and fall, as the kinetic energy of the mass falls and rises. The change in potential energy, dV , is

$$dV = -f dx = kx dx, \quad (8)$$

so that upon integrating,

$$V = \frac{1}{2}kx^2 + \text{constant}. \quad (9)$$

The constant of integration may be set equal to zero. This potential energy function is shown as the parabolic line in Figure 1(b). The kinetic energy of this harmonic oscillator is given by

$$E_K = \frac{1}{2}mv^2 = \frac{1}{2}m \left(\frac{dx}{dt} \right)^2 = \frac{m}{2}(A\omega)^2 \cos^2 \omega t \quad (10)$$

This function is also plotted in Figure 1(b). The total constant energy, E , of the system is given by

$$E = V + E_K = \frac{1}{2}kx^2 + \frac{m}{2}(A\omega)^2 \cos^2 \omega t = \frac{1}{2}kA^2 \sin^2 \omega t + \frac{m}{2}(A\omega)^2 \cos^2 \omega t, \quad (11)$$

where we have substituted equation 6 for x . Substituting equation 4 for ω^2 , we can write

$$E = \frac{1}{2}A^2k (\sin^2 \omega t + \cos^2 \omega t) = \frac{1}{2}A^2k \quad (12)$$

The total energy is thus a constant and is shown as a horizontal line in Figure 1(b). At the limits of oscillation, where the mass is reversing its direction of motion, its velocity will be momentarily equal to zero, and its momentary kinetic energy will therefore also be zero, meaning that the potential energy will be maximized and equal to the total energy of the system at the two turning points. As the oscillator begins to undergo acceleration away from the turning points, the kinetic energy will increase, and the potential energy will decrease along the curve, V , as shown in Figure 1(b).

If the spring constant, k , should not be constant, but should vary slightly from a constant value as x changes, we would be dealing with an *anharmonic oscillator*. In most cases, an anharmonic oscillator may be closely approximated by the harmonic oscillator equations for small displacements from equilibrium, x .

Soon we will be comparing the quantum harmonic oscillator with the classical harmonic oscillator, and the probability of finding the mass at various values of x will be of interest. We now calculate this probability for the classical harmonic oscillator.

The probability of finding the mass, m , at any given value of x is inversely proportional to the velocity, v , of the mass. This is reasonable, since the faster the mass is moving, the less likely it is to observe the mass. Hence, we expect that the probability of observing the mass will be have

a *minimum* at $x = 0$, where the velocity is at a maximum, and conversely will exhibit *maxima* when $x = \pm A$. From equation 7 we see that

$$v(x) = \frac{dx}{dt} = A\omega \cos \omega t, \quad (13)$$

so that

$$\mathcal{P}(x)dx \propto \frac{dx}{A\omega \cos \omega t}, \quad (14)$$

where $\mathcal{P}(x)dx$ is the probability of finding the mass between x and $x + dx$. Note that since x is a continuous variable that we define $\mathcal{P}(x)dx$ as the probability and $\mathcal{P}(x)$ is called the *probability density*, which is the probability per unit length, in this case. We note that at the turning points of the oscillation, when $1/4$ or $3/4$ of a cycle has occurred, that $t = \frac{\pi}{2\omega}$ or $t = \frac{3\pi}{2\omega}$ and at these points $\cos \omega t$ goes to zero, with $\frac{1}{v}$ going to infinity. We know that the probability of finding the mass at the end points must be a maximum, *but must not be infinite*. The reason that $\mathcal{P}(x)$ remains finite is that dx in equation 14 always has finite width, therefore, $\mathcal{P}(x)$ is not defined exactly at a point. For example, at $t = \frac{\pi}{2\omega}$, $\mathcal{P}(x)$ is evaluated over the range $-A < x < -A + dx$.

This probability density function as a function of the x -coordinate, $\mathcal{P}(x)$, is plotted along with the velocity, v in Figure 2. The probability density is a smooth function over the range of x available to the oscillator and has exactly one minimum at $x = 0$. We will soon find that this intuitive classical behavior is not obeyed by the quantized harmonic oscillator. In fact, for the quantum oscillator in the ground state we will find that $\mathcal{P}(x)$ has a *maximum* at $x = 0$.

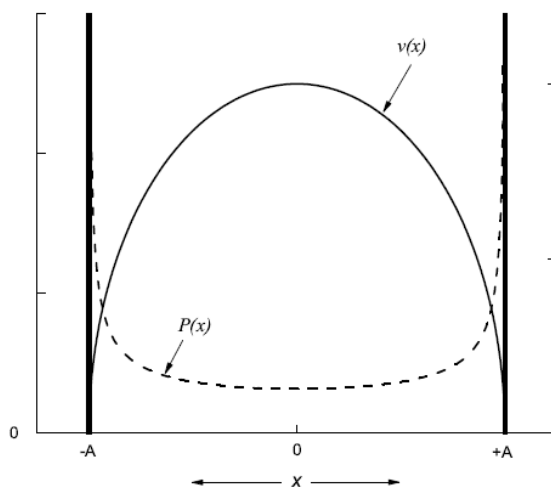


Figure 2: Probability Density, $\mathcal{P}(x)$, for Classical Harmonic Oscillator at Various Displacements, x . $\mathcal{P}(x)$ is plotted as the dashed line and the velocity, $v(x)$ is plotted as the solid curve. The two vertical lines give the limits of the oscillator motion. Note that $\mathcal{P}(x) \propto \frac{1}{v(x)}$.

The Quantum Harmonic Oscillator

The quantum harmonic oscillator is a very important problem in quantum mechanics. For example, it serves as a first-order approximation for the bond vibrational problem in diatomic and (with

coupling) polyatomic molecules. We will examine the quantum harmonic oscillator in some detail, comparing it with what we know about the classical harmonic oscillator from the previous section. The potential energy function for the quantum harmonic function is the same as for the classical harmonic oscillator, namely, $V = 1/2kx^2$. Thus, in the quantum Hamiltonian is

$$H_{op} = E_{Kop} + V_{op} \quad (15)$$

and we may write the Schrödinger equation as

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2} kx^2 \psi = E\psi \quad (16)$$

The general solution to this problem (which we will not derive) can be written as

$$\psi_n(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^n n!}\right)^{1/2} H_n(y) e^{-y^2/2}, \quad (17)$$

where $n = 0, 1, 2, \dots$ is the quantum number, $\alpha = \frac{m\omega}{\hbar}$, $y = \alpha^{1/2}x$, and $H_n(y)$ is a Hermite polynomial of order n . The first few Hermite polynomials are

$$H_0(y) = 1 \quad (18)$$

$$H_1(y) = 2y \quad (19)$$

$$H_2(y) = 4y^2 - 2 \quad (20)$$

$$H_3(y) = 8y^3 - 12y \quad (21)$$

$$H_4(y) = 16y^4 - 48y^2 + 12 \quad (22)$$

Hermite polynomials of any order can be calculated from the recursion relation

$$H_{n+1}(y) = 2yH_n(y) - 2nH_{n-1}(y). \quad (23)$$

The allowed energies (eigen energies) for the quantum harmonic oscillator are

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad (24)$$

and since $\omega = 2\pi\nu$,

$$E_n = \left(n + \frac{1}{2}\right) h\nu. \quad (25)$$

Using equation 4 for ω , we may write

$$E_n = \left(n + \frac{1}{2}\right) \hbar \left(\frac{k}{m}\right)^{1/2}. \quad (26)$$

The ground state wavefunction for the quantum harmonic oscillator can be obtained by substituting $H_0(y)$ from equation 18, using $y = \alpha^{1/2}x$, into equation 17,

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}}. \quad (27)$$

Likewise, the first and second excited state wavefunctions are

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} \quad (28)$$

$$\psi_2(x) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}. \quad (29)$$

Figure 3 shows the first few allowed energy levels for the quantum harmonic oscillator. Also shown are the wavefunctions, ψ_n and the probability densities, $|\psi_n|^2$ for the levels $n = 0, 1, 2$. The

equally spaced set of allowed vibrational energy levels observed for a quantum harmonic oscillator is not expected classically, where all energies would be possible. The quantization of the energy levels of the harmonic oscillator is similar in spirit to the quantization of the energy levels for the particle in a box, except that for the harmonic oscillator, the potential energy varies in a parabolic manner with the displacement from equilibrium, and the walls of the “box” therefore are not vertical. We might say, in comparison to the “hard” vertical walls for a particle in a box, that the walls are “soft” for the harmonic oscillator. In addition, the spacing between the allowed energy levels for the harmonic oscillator is a constant value, $h\nu$, whereas for the particle in a box, the spacing between levels rises as the quantum number, n , increases.

There is another interesting feature seen in Figure 3. For the lowest allowed energy, when $n = 0$, we see that the quantum harmonic oscillator possesses a zero-point energy of $\frac{1}{2}h\nu$

This too is reminiscent of the particle in a box, which displays a finite zero-point energy for the first allowed quantum number, $n = 1$. This lowest allowed zero-point energy is unexpected on classical grounds, since all vibrational energies, down to zero, are possible in the classical oscillator case.

Recall that we developed an expression for the probability of observing a classical harmonic oscillator between x and $x + dx$ and found that this probability is inversely proportional to the velocity of the oscillator (see equation 14). The corresponding probability for a quantum harmonic oscillator in state n is proportional to $| \psi_n |^2$. We now compare the probability densities of classical and quantum harmonic oscillators. Recall that the ground state for the classical oscillator has zero energy (and zero motion), whereas the quantum oscillator in the ground state has an energy of $\frac{1}{2}h\nu$. Therefore, it does not make sense to compare classical and quantum oscillators in their ground states. We can however directly compare probability densities by comparing quantum and classical oscillators having the same energy. Equating the quantum and classical oscillator

energies, we have

$$E_n = \left(n + \frac{1}{2}\right) h\nu = \frac{1}{2} A^2 k, \quad (30)$$

where A is the classical amplitude, or limit of motion. Solving for A , we have

$$A = \left[\frac{2h\nu}{k} (2n + 1) \right]^{1/2} \quad (31)$$

That is, a classical oscillator with energy E_n will oscillate between $x = \pm A$, with A given by equation 31. The quantum and classical probability densities for $n = 0, 2, 5$, and 20 are plotted in Figure 4.

We see from equation 27 that $|\psi_0|^2$ is a Gaussian function with a maximum at $x = 0$. This is plotted in the upper left panel of Figure 4. Contrast this behavior with the classical harmonic oscillator, which has a minimum in the probability at $x = 0$ and maxima at the turning points. Also note that the limits of oscillation are strictly obeyed for the classical oscillator, shown by the vertical lines. In contrast, the probability density for the quantum oscillator “leaks out” beyond the $x = \pm A$ classical limits. *The quantum harmonic oscillator penetrates beyond the classical turning point! This phenomenon is akin to the quantum mechanical penetration of a finite barrier seen previously.* Thus, the probability densities for the quantum and classical oscillators for $n = 0$ have almost opposite shapes and very different behavior. Next, we compare the classical and quantum oscillators for $n = 2$ (top right panel in Figure 4). Note that the probability density for the quantum oscillator now has three peaks. In general, the quantum probability density will have $n+1$ peaks. In addition to having $n+1$ maxima, the probability density also has n minima. Remarkably, these minima correspond to zero probability! *This means that for a particular quantum state n there will be exactly n forbidden locations where the wave function goes to zero (nodes).* This is very different from the classical case, where the mass can be at any

location within the limits $-A \leq x \leq A$. Note also that the middle peak centered at $x = 0$ has a smaller amplitude than the outer two peaks. Thus, for $n = 2$ we are beginning to see behavior that is closer in spirit to the classical probability density, that is, the probability of observing the oscillator should be greater near the turning points than in the middle. The classical probability density is essentially the same for all energies, but is just “stretched” to larger amplitudes for higher energies. For $n = 5$, shown in the lower left panel of Figure 4, we see the continued trend that the peaks near $x = 0$ are smaller than the peaks near the edges. Note that the probability densities continue to extend past the classical limits of motion, but die off exponentially. Finally, for $n = 20$ note that the gaps between the peaks in the probability density become very small. At large energies the distance between the peaks will be smaller than the Heisenberg uncertainty principle allows for observation. In other words, we will no longer be able to distinguish the individual peaks. The probability will be smeared out. You should be able to see that for $n = 20$ an appropriate average of the quantum probability density closely approximates the classical behavior probability density. The region of non-zero probability outside the classical limits drops very quickly for high energies, so that this region will also be unobservable as a result of the uncertainty principle. Thus, the quantum harmonic oscillator smoothly crosses over to become a classical oscillator. This crossing over from quantum to classical behavior was called the “correspondence principle” by Bohr.

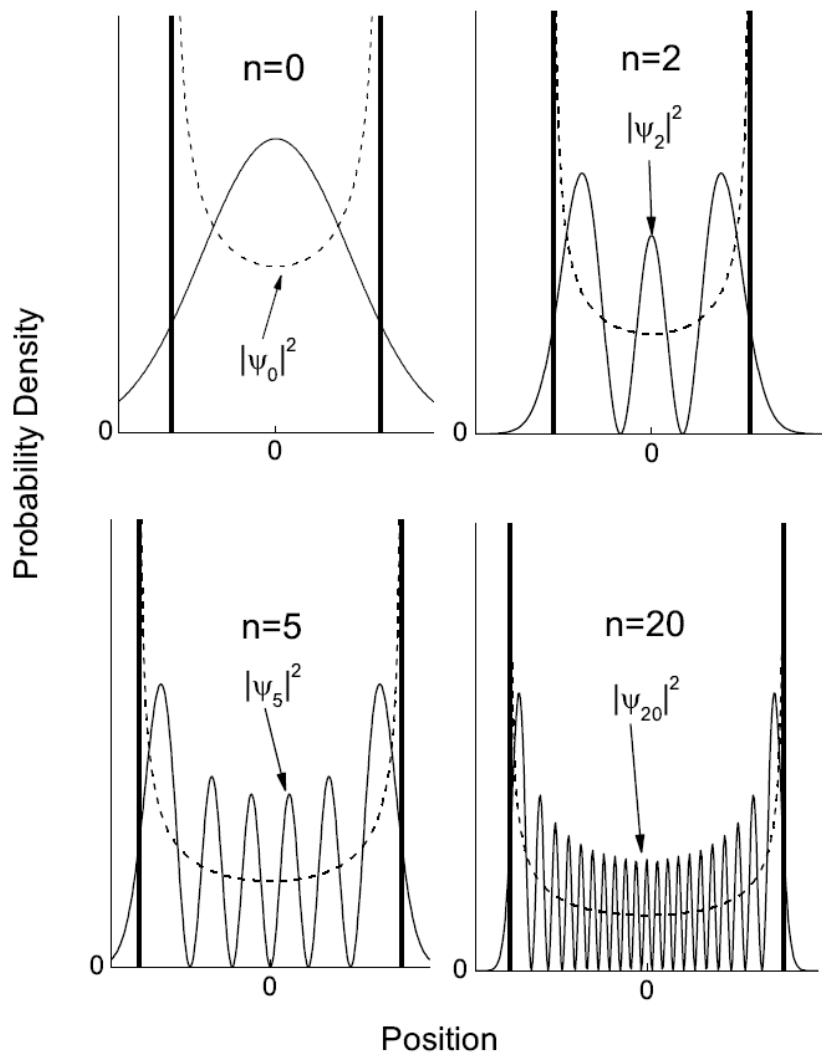


Figure 4: Probability Densities for Quantum and Classical Harmonic Oscillators. The probability densities for quantum harmonic oscillators, $|\psi_n(x)|^2$, are plotted as solid lines for the quantum numbers $n = 0, 2, 5, 20$. The probability densities of the classical harmonic oscillators having the same energies as the quantum oscillators are plotted as dashed lines. The classical limits of motion are shown by the vertical lines.

The Quantized Rigid Rotor—Three-Dimensional

Our reason for studying the idealized rigid rotor is to ultimately apply our understanding to molecules that rotate in a quantized fashion. At this stage of our development, the student should be thinking about a diatomic molecule that is rotating like a dumbbell in space. A schematic of a carbon monoxide molecule is shown in Figure 7. This diatomic molecule possesses a single moment of inertia, $I = m_1 r_1^2 + m_2 r_2^2$, where m_1 and m_2 are the masses of the atoms, and r_1 and r_2 are the distances of these masses from the center of mass of the molecule. In the three dimensional case, the diatomic molecule can tumble in space, or more specifically its plane of rotation can occur in any plane in space. The physical condition we have previously considered in which rotation occurs in a fixed plane (planar rotor) does not apply. We will not derive the equations related to the three-dimensional rigid rotor but will give the result in equation 45

$$E_{\text{rot}}^{3D} = J(J+1) \frac{\hbar^2}{2I} \quad (45)$$

where the quantum number $J = 0, 1, 2, \dots$

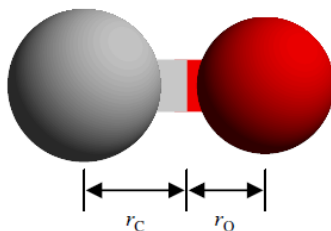


Figure 7: Schematic of a Carbon Monoxide Molecule. The distance of each atom from the center of mass is shown, where r_C is the distance from the carbon atom (light sphere) to the center of mass and r_O is the distance from the oxygen atom (dark sphere) to the center of mass.

A plot of the allowed rotational energy levels for a diatomic molecule is shown in Figure 8 as a function of the quantum number, J . It may be seen that as J increases, the spacing between allowed rotational quantum states increases. If we let J be the rotational quantum number of a particular state, with $(J-1)$ the rotational quantum number of the next lower allowed state, then one may calculate that the spacing between adjacent levels increases by the amount $\frac{2J\hbar^2}{2I}$, which will be called $2JB$ where B is the rotational constant, given by

$$B = \frac{\hbar^2}{2I}. \quad (46)$$

This will become important when we discuss spectroscopic transitions between neighboring rotational states. [The student should prove $\Delta E = E_J - E_{J-1} = 2JB$].

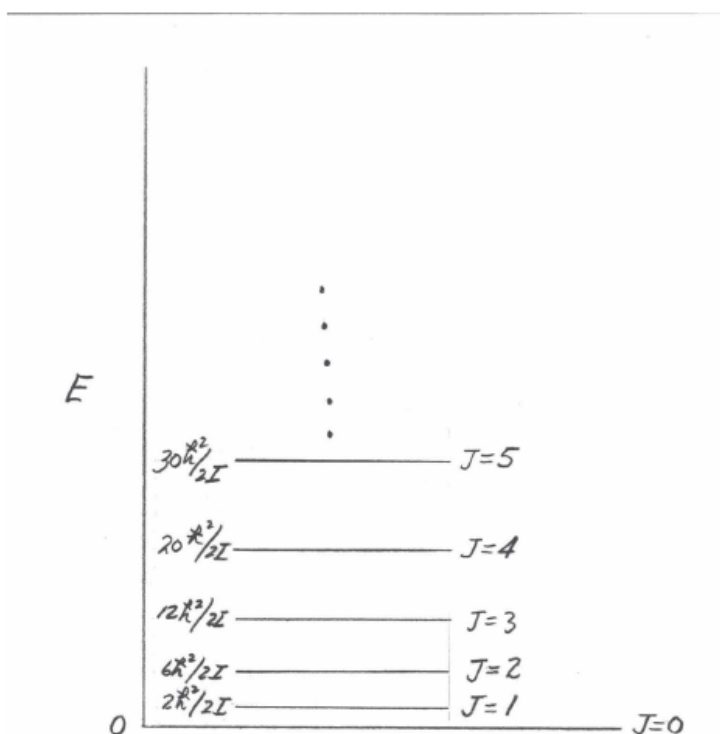


Figure 8: Allowed Energy Levels for the Rotations of a Diatomic Molecule.

Possible Questions

PART- A Questions

(Each questions carries one mark)

- The power emitted per unit area of the surface of a black body is directly proportional to the fourth power of its absolute temperature, the law is
 - Stefan Boltzmann law**
 - Weins displacement law
 - Planck's law
 - Jean's law
- Evidence in favour of the particle nature of radiation
 - Diffraction of radiation
 - Compton effect**
 - polarization
 - interference
- Black body radiation has a characteristic continuous spectrum of radiation which depends upon
 - Body's temperature**
 - Nature of the body
 - Colour of the body
 - Density of the body

4. The spectrum of black-body radiation at any temperature is related to the spectrum at any other temperature
 - a. Stefan Boltzmann law b. **Weins displacement law**
 - c. Planck's law d. Jean's law
5. In one dimensional box problem the potential energy of the particle outside the box is
 - a. zero b. unity c. **infinity** d. fractional
6. The energy levels of the particle in the box are
 - a. quantized b. randomized c. dispersed d. Not-quantized
7. The theory of rigid rotor in space is useful in dealing with
 - a. **Rotational spectra of diatomic molecules** b. Vibrational spectra of diatomic molecules
 - c. IR spectra of diatomic molecules d. Raman spectra of diatomic molecules
8. In the Hook's law $f = -kx$, k is called
 - a. **Force constant** b. Gas constant
 - c. Boltzmann constant d. Faraday's constant
9. An one electron system whose potential field is not spherically symmetrical
 - a. Hydrogen atom b. **Hydrogen atom in electric field**
 - c. Hydrogen molecule d. Helium molecule
10. The method to obtain approximate solutions to the wave equation
 - a. **Perturbation method** b. Normalization of the wave function
 - c. Making the wave functions orthogonal d. Making the wave functions orthonormal
11. The method applicable for a system which wave functions may be guessed
 - a. Perturbation method b. **Variation method**
 - c. Normalization of the wave function d. Making the wave functions orthogonal
12. Write the energy level for the free particle in motion
 - a. $E_n = 2n - 1/2$ b. $E_n = n^2$ c. **E_n is continuous** d. $E_n \propto n^2$
13. The shape of BeCl_2 molecules is
 - a. **Linear** b. Triangular planar c. Tetrahedral d. octahedral
14. Example for tetrahedral molecule
 - a. BeCl_2 b. boron trifluoride c. **methane** d. phosphorous pentachloride
15. If the symmetry element is the 'plane of symmetry' then the corresponding symmetry operation is
 - a. Doing nothing b. **reflection** c. Inversion of all coordinates
 - d. Rotation through an angle of $360/n$ about an axis where 'n' is the order of the axis
16. For the symmetry operation "rotation" the corresponding symmetry element is
 - a. Identity element b. Plane of symmetry
 - c. Centre of symmetry d. **Proper axis of symmetry**
17. The basic theorem is concerned with the elements of the matrices constituting the irreducible representation of a group is called
 - a. Faradays theorem b. **The great orthogonality theorem**
 - c. Normalized theorem d. Van der Waals theorem
18. Character tables are constructed using
 - a. Symmetry elements b. **Orthogonality theorem**
 - c. Symmetry operations d. Irreducible operations
19. The corresponding matrix for the operation E is
 - a. Zero matrix b. Square matrix c. Diagonal matrix d. **Unit matrix**

20. Reducible representation is also called as
- Total character**
 - Symmetry elements
 - Symmetry operations
 - Total elements of symmetry

PART- B Questions

(Each questions carries six marks)

21. (a). (i) Give an explanatory note on time dependent Schrodinger equation.
(ii) S.T. Weins and Rayleigh Jeans law are the limiting cases of planks Expression, Explain.
(OR)
(b). Give a detailed account on black body radiation.
22. (a) Compare the classical mechanics and quantum mechanics with particle in one dimensional box.
(OR)
(b) Derive the equation for particle in three dimensional box and separation of variables.
23. (a). Give an account on the applications of variation method.
(OR)
(b) (i) Explain radial distribution functions.
(ii) Explain the perturbation method to anharmonic oscillator.
24. a. Write notes on
(i) What is a group?
(ii) What are the defining properties of a group?
(iii) Define class.
(OR)
b. Write notes on improper rotation and plane of symmetry with suitable examples.
25. (a) (i) What are the relationships between reducible and irreducible representation of the group.
(ii) What are the Properties of irreducible representation?
(OR)
(b) Explain the symmetry selection rules for infra-red and Raman spectra.

PART- C Question

(Each Question carries ten marks)

26. Differentiate variation method and perturbation method with an example?



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(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2017 & onwards)
Quantum Chemistry

Multiple Choice Questions for Unit II

S. No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	The solution of the problem of the rigid rotator gives us directly the solution of the	angular momentum operator	Lapalacian operator	Hermitian operator	Position operator	angular momentum operator
2	Two atoms of mass m_1 and m_2 rigidly joined by a weightless link of length R is a	Rigid rotator	Simple harmonic oscillator	Particle in one dimensional box	Particle in three dimensional box	Rigid rotator
3	The theory of rigid rotor in space is useful in dealing with	Rotational spectra of diatomic molecules	Vibrational spectra of diatomic molecules	IR spectra of diatomic molecules	Raman spectra of diatomic molecules	Rotational spectra of diatomic molecules
4	A diatomic molecule in space where the bond length is assumed to remain unchanged during rotation is a	Rigid rotator	Simple harmonic oscillator	Particle in one dimensional box	Particle in three dimensional box	Rigid rotator
5	$E_0 = \frac{1}{2} h\nu$ is the zero point energy of	Simple harmonic oscillator	Rigid rotor	Particle in one dimensional box	Particle in three dimensional box	Simple harmonic oscillator
6	$V(x) = \frac{1}{2} kx^2$, this is an equation of a	Parabola	Hyperbola	circle	Straight line	Parabola
7	Force constant k in Hook's law is high for	Single bond	Double bond	Triple bond	H-bond	Triple bond

8	Force constant k in Hook's law depends upon the	Bond strength between two atoms	Molecular weight of the two atoms	Acceleration due to gravity	Viscosity of the participating atoms	Bond strength between two atoms
9	In the Hook's law $f = -kx$, k is called	Force constant	Gas constant	Boltzmann constant	Faraday's constant	Force constant
10	According to Hooke's law the force 'f' acting on a molecule is given by	$-kx$	mgh	mv	$\frac{1}{2} mv$	$-kx$
11	A diatomic vibrating molecule can be represented by a simple model called	Simple harmonic oscillator	Rigid rotor	Particle in one dimensional box	Particle in three dimensional box	Simple harmonic oscillator
12	The quantum number 'n' is called	Principal quantum number	Azimuthal quantum number	Magnetic quantum number	Angular momentum quantum number	Principal quantum number
13	In the particle in one dimensional problem, The property of orthogonality between any two different states ensures that	The various states are truly independent	The various states are dependent	One state is independent and the other is dependant	All are dependent and still do not interfere with each other	The various states are truly independent
14	The wave functions for different states of the problem, the particle in one dimensional box system are	orthogonal	normal	metagonal	paragonal	orthogonal
15	Molecules are known to absorb radiation in which region of the electromagnetic spectrum:	Ultra violet	NMR	Mass	heat	Ultra violet

16	Which of the following is NOT a correct aspect of the Born-Oppenheimer approximation	The electrons in a molecule move much faster than the nuclei.	Excited electronic states have the same equilibrium internuclear distance as the ground electronic state.	The electronic and vibrational motions of a molecule are approximately separable	The typical amplitude of nuclear vibration is much smaller than that characterizing the motion of electrons.	Excited electronic states have the same equilibrium internuclear distance as the ground electronic state.
17	oxygen, just above it in the periodic table, has only a valence of 2. Why is this?	The sulfur atom can access d-orbitals	Breakdown of the Pauli principle	Breakdown of the Born-Oppenheimer approximation	Excited	The sulfur atom can access d-orbitals
18	The ground state of the ozone molecule O ₃ has the following shape Sulfur apparently shows a valence of 6 in the molecule SF ₆ , whereas	linear	tetrahedral	bent	equilateral triangle	bent
19	excited state of the helium atom has the term symbol	¹ S ₀	³ S ₁	2s ₂	He ⁺	³ S ₁
20	The ionization energy for hydrogen atom is 13.6 eV. The ionization energy for the ground state of L ⁱ⁺⁺ is approximately	27.2	40.8	54.4	122.4 eV	122.4 eV
21	The expectation value of 1/r in the ground state of the hydrogen atom equals	a ₀	(3/2)a ₀	a ₀ /4π	1/a ₀	1/a ₀

22	Which of the following statements about the hydrogen atom ground state is INCORRECT:	It is described by the quantum numbers $n = 1, l = 0; m = 0$.	The electron's angular momentum equals \hbar .	The wavefunction is spherically symmetrical.	The wavefunction decreases exponentially as a function of r .	The electron's angular momentum equals \hbar .
23	For real atomic orbitals with quantum numbers n, l , the total number of nodal surfaces, radial plus angular, equals	n	$n - 1$	$n - l - 1$	$n + l$	$n - l$
24	The orbital degeneracy (excluding spin) of hydrogen atom energy levels equals	n	$n + 1$	$2n + 1$	n^2	n^2
25	For the hydrogen atom, which of the following orbitals has the lowest energy	4p	4d	4f	They all have the same energy	They all have the same energy
26	The atomic orbital illustrated to consists of two lobes	2p	3s	3p	3d	3d
27	Spherical polar coordinates are used in the solution of the hydrogen atom Schrödinger equation because	the Laplacian operator has its simplest form in spherical polar coordinates.	cartesian coordinates would give particle-in-a-box wavefunctions.	the Schrodinger equation is then separable into 3 ordinary differential equations.	otherwise the atomic orbitals would violate the Pauli exclusion principle.	the Schrodinger equation is then separable into 3 ordinary differential equations.
28	A hydrogen atom radiates a photon as it falls from a 2p level to the 1s level. The wavelength of the emitted radiation equals	22.8	91.2	121.6	182.4	121.6
29	The illustrated wavefunction represents the state of the linear harmonic oscillator with $n=$	1	2	3	5	5

30	The energy levels of the linear harmonic oscillator are	all non degenerate	n-fold degenerate	$(n + 1/2)$ -fold degenerate	$(2n + 1)$ -fold degenerate	all non degenerate
31	The corresponding eigenvalue equals	0	$\hbar k$	$i\hbar k$	$\hbar^2 k^2$	$\hbar k$
32	Which of the following is NOT a solution of the differential equation $y''(x) + k^2 y(x) = 0$	$\exp(i k x)$	$\exp(j k x)$	$\sin k x$	$\cos k x$	$\exp(j k x)$
33	Which of the following is NOT a correct consequence of the Heisenberg	The shorter the lifetime of an excited state of an atom, the less accurately can its energy be measured.	An electron in an atom cannot be described by a well-defined orbit.	The momentum of an electron cannot be measured exactly.	Measurement of one variable in an atomic system can affect subsequent measurements of other variables	The momentum of an electron cannot be measured exactly.
34	Planck's constant has the same as	angular momentum number	the Hamiltonian	frequency	quantum	angular momentum number
35	A diatomic molecule is initially in the state where $l = 5$ is a spherical harmonic. What is the probability of obtaining result $l = 5$?	36/1444	9/38	13/38	34/38	13/38
36	A particle with energy E is in a time dependent double well potential shown in figure, which of the following statement about the particle is not correct ?	The particle will always be in a bound state	The probability of finding the particle in one well will be time independent	The particle will be confined to any one of the well's	The particle can tunnel from one well to other and back	The particle will be confined to any one of the well's

37	Consider the following statements. A particle of energy E is incident from the left on a potential step of height V_0 at $x=0$ 1. if $E < V_0$, wave function of the particle is zero for $x > 0$ 2. if $E < V_0$, wave function is not zero for $x > 0$ 3. if $E > V_0$, reflection coefficient is not zero. Which of the statements given above are correct	1 only	2 only	1 and 2 only	2 and 3 only	2 and 3 only
38	The eigen function of hydrogen atom contain which of the following ? 1. Legendure polynomials 2. Laguerre polynomials 3. Hermite polynomials. Select the correct answer using the code given below	1,2 and 3	1 & 2	1 only	2 only	1 & 2
39	The wave function for a particle in one-dimensional potential well is given by $\sqrt{2/a} \sin n\pi x/a$, $0 < x < a$, when a potential of $V(x) = \cos \pi x/a$ is applied, the change in first order energy is	zero	a/π	$2\pi/a$	$2\pi/a$	zero
40	If perturbation $H' = ax$, where a is a constant, is added to infinite square well potential $V(x) = 0$ for $0 \leq x \leq \pi$, $V(x) = \infty$ otherwise. The correction to the ground state energy to first order in a is	$a\pi/2$	$a\pi$	$a\pi/4$	$a\pi/\sqrt{2}$	$a\pi/2$
41	A particle constrained to move along the x -axis is described by the wave function $\Psi(x) = 2x$; $0 < x < 1$ $\Psi(x) = 0$; elsewhere. What is the probability of finding the particle within $(0,0.4)$	0.85	0.085	0.0085	0.00085	0.085

42	For a particle of mass m in a one-dimensional box of length l , what is the average of momentum P_x for the ground state	zero	$h/(2l)$	h/l	$h/(2\pi l)$	$h/(2l)$
43	If n represents the number of eigen states of a hydrogen atom, then its discrete energy levels are proportional to	n	n^2	$1/n$	$1/n^2$	$1/n^2$
44	A particle of mass m is in a simple harmonic oscillator potential $V = x^2$. If the ground state wave function is Ae^{-ax^2} , what is the expression for constant a equal to	$2\pi(m/2)^{1/2}/h$	$2\pi(1/m)^{1/2}/h$	$h(m/2)^{1/2}/2\pi$	$h(m)^{1/2}/2\pi$	$2\pi(m/2)^{1/2}/h$
45	A particle of mass m is confined in the ground state of a one-dimensional box extending from $x=-2L$ to $x=+2L$. The wave function of the particle in this state $\Psi(x) = \Psi_0 \cos \pi x/4L$, where Ψ_0 is constant. The energy of eigen value corresponding to this state is	$h^2\pi^2/2mL^2$	$h^2\pi^2/4mL^2$	$h^2\pi^2/16mL^2$	$h^2\pi^2/32mL^2$	$h^2\pi^2/32mL^2$
46	The wave function of a particle in a box of length L is $\Psi(x) = \sqrt{2}/L \sin \pi x/L$, $0 < x < L$, $\Psi(x)=0$ $x < 0$ & $x > L$ the probability of the particle finding in the region $0 < x < L/2$ is	0.40%	0.30%	0.20%	0.50%	0.50%
47	A free electron moving without any restriction has the continuous energy spectrum	Line spectrum	continuous energy spectrum	Discrete energy spectrum	Band spectrum.	continuous energy spectrum
48	The occurrence of zero point energy in one dimensional box problem is in accordance with the	Pauli's exclusion principle	Heisenberg's uncertainty principle	Hund's rule	Aufbau principle	Heisenberg's uncertainty principle

49	The zero point energy equation shows that the electron inside the box is not at rest, hence	The position of the electron can be precisely known	The momentum of the electron cannot be precisely known	The momentum of the electron can be precisely known	The velocity of the electron cannot be precisely known	The momentum of the electron cannot be precisely known
50	The zero point energy equation shows that the electron inside the box is not at rest, hence	The position of the electron can be precisely known	The position of the electron cannot be precisely known	The momentum of the electron can be precisely known	The velocity of the electron cannot be precisely known	The position of the electron cannot be precisely known
51	The value of zero is not acceptable for the value of 'n' because	The wave function will become unity	The wave function will become zero	The wave function will become infinite	The wave function will become well behaved	The wave function will become zero
52	The electron inside the box is	Not at rest at 0°K.	Not at rest at 0°C	Not at rest at 298K	Not at rest at 300K	Not at rest at 0°K.
53	The value of the arbitrary constant A in the particle in a box problem is	Zero	one	two	three	Zero
54	The value of wave function at the walls of the box is	Zero	one	two	three	Zero
55	The value of wave function out side the box is	Zero	one	two	three	Zero
56	The value of the arbitrary constant B in the particle in a box problem is	Square root of 2/a	Square of 2/a	Cube root of 2/a	Cube of 2/a	Square root of 2/a
57	The energy levels of the particle in the box are	quantised	randomised	dispersed	Not-quantised	quantised
58	The possible values of 'n' in the schrodinger's equation can have values	1,2,3,4	0,1,2,3....	zero	0,2,4,	1,2,3,4

59	In one dimensional box problem the potential energy of the particle in the boundaries of the box is	zero	unity	infinity	fractional	zero
60	In one dimensional box problem the potential energy of the particle outside the box is	zero	unity	infinity	fractional	infinity

UNIT – III
Approximation and Variation Methods

Schrodinger equation for the H-atom (or H-like species)- separation of variables - energy levels. Radial distribution functions - orbitals and orbital shapes. Probability density and radial distribution functions.

Need for approximation methods. The perturbation theory- application of perturbation method to systems such as anharmonic oscillator and He-atom.

The variation method - application of variation method to systems such as anharmonic oscillator and He-atom.

$$\begin{aligned} H |n\rangle &= E_n |n\rangle \\ H |m\rangle &= E_m |m\rangle \end{aligned}$$

We can multiply each equation with $\langle n|$ or $\langle m|$ from the left and obtain the following terms:

$$\begin{aligned} \langle n| H |n\rangle &= E_n \langle n|n\rangle = E_n \\ \langle n| H |m\rangle &= E_m \langle n|m\rangle = 0 \\ \langle m| H |n\rangle &= E_n \langle m|n\rangle = 0 \\ \langle m| H |m\rangle &= E_m \langle m|m\rangle = E_m \end{aligned}$$

In matrix notation this would be:

$$\begin{aligned} H_{nn} &= E_n & H_{nm} &= 0 \\ H_{mn} &= 0 & H_{mm} &= E_m \end{aligned}$$

And thus the Hamiltonian matrix looks like:

$$\mathbf{H} = \begin{bmatrix} H_{nn} & H_{nm} \\ H_{mn} & H_{mm} \end{bmatrix} = \begin{bmatrix} E_n & 0 \\ 0 & E_m \end{bmatrix}$$

In perturbation theory we will be concerned with Hamiltonians of the form:

$$H = H^{(0)} + H^{pert}$$

where $H^{(0)}$ is our original Hamiltonian with well-defined eigenstates, and H^{pert} is a perturbing term. The matrix elements now become:

$$\mathbf{H} = \begin{bmatrix} H_{nn}^{(0)} + H_{nn}^{pert} & H_{nm}^{(0)} + H_{nm}^{pert} \\ H_{mn}^{(0)} + H_{mn}^{pert} & H_{mm}^{(0)} + H_{mm}^{pert} \end{bmatrix} = \begin{bmatrix} E_n + H_{nn}^{pert} & H_{nm}^{pert} \\ H_{mn}^{pert} & E_m + H_{mm}^{pert} \end{bmatrix}$$

We see that the off-diagonal elements are no longer zero for this new Hamiltonian. Note that the total Hamiltonian is still hermitian, which implies that H^{pert} must be hermitian as well. We thus have:

$$(H_{nm}^{pert})^* = (H_{mn}^{pert})^\dagger = H_{mn}^{pert}$$

We will use these matrix elements throughout the remainder of the Chapter.

Idea Behind Perturbation Theory

Perturbation theory assumes that the solution is close to an exact solution. It describes the system in terms of a simplified Hamiltonian to which we know the wavefunctions and energies, with a small correction to account for the actual complexity of the system. We can therefore write the total Hamiltonian as:

$$H = H^{(0)} + H^{pert}$$

Here $H^{(0)}$ is the Hamiltonian with known energies and wavefunctions, and H^{pert} is the correction, or perturbation to the simplified Hamiltonian. The total Hamiltonian now gives a full description of the system. How do we find the wavefunctions? Generally, we can use the known solutions $|n\rangle$ as a basis set and composing the new solutions from a linear combinations of $|n\rangle$:

$$\Psi = \sum_n c_n |n\rangle$$

This always holds, but it is generally not so straightforward to find the wavefunctions in this fashion. It is more convenient to proceed in steps and find solutions of converging accuracy to the actual wavefunction. Perturbation theory therefore assumes the following. The perturbation Hamiltonian can be written as an expansion, with each element giving a slight correction to the former:

$$\begin{aligned} H &= H^{(0)} + H^{pert} \\ H^{pert} &= \lambda H^{(1)} + \lambda^2 H^{(2)} + \dots \end{aligned}$$

where λ is a parameter that indicates the order of the correction. We assume that the energy can be written accordingly:

$$\begin{aligned} E &= E_n + E_n^{pert} \\ E_n^{pert} &= \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned}$$

with $E_n^{(1)}$ the first order correction to the unperturbed energy and $E_n^{(2)}$ the second order correction to the unperturbed energy. The energy is thus close to the unperturbed energy E_0 and we add subsequent orders to arrive at a better approximation for the actual energy. Similarly, we can approach the actual wavefunction step by step as:

$$\begin{aligned} \Psi &= \Psi_n + \Psi^{pert} \\ \Psi^{pert} &= \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots \end{aligned}$$

here, the correction to a state $|n\rangle$ can be written as

$$\begin{aligned} \Psi_n &= |n\rangle \\ \Psi_n^{(1)} &= \sum_n a_n^{(1)} |n\rangle \\ \Psi_n^{(2)} &= \sum_{n'} a_{n'}^{(2)} |n'\rangle \end{aligned}$$

Subsequent orders give a better description of the actual wavefunction. Most commonly, we will truncate the expansion after one or two corrections if we are satisfied with the result, as higher orders give only incremental improvements of the actual wavefunction.

We learned that perturbation theory can be used to calculate the energy and wavefunction for systems that are somewhat different from simple case scenarios. With perturbation theory we can calculate the effect of a small perturbation to the Hamiltonian on the energies and wavefunctions, to arrive at a better description of the system. By looking at a two level system, we saw that:

- A perturbation tends to increase the energy splitting of two levels; the lower level goes down while the higher level goes up.
- A perturbation will mix the unperturbed states to arrive at a new wavefunction which gives a better description of the new system.

Variation Theory

Variation theory is another powerful method for finding wavefunctions and energies in systems that do not lend themselves for a direct analytical solution. Variation theory is a trial-and-error method in which we vary a trial wavefunction so that it minimizes the ground state energy. We make use of the following condition:

$$E = \frac{\int \psi_{trial}^* H \psi_{trial} dV}{\int \psi_{trial}^* \psi_{trial} dV} \geq E_0$$

That is, the expectation value of the energy using an arbitrary wavefunction is equal or larger than the ground state energy. This condition is easily verified by writing the (normalized) trial wavefunction in terms of the linear combination of the Hamiltonian's basis set $\psi_{trial} = \sum_n c_n |n\rangle$ and calculating the integral $\langle H \rangle$:

$$\begin{aligned} \langle H \rangle &= \sum_{n,n'} c_n^* c_{n'} \langle n | (H) | n' \rangle \\ &= \sum_{n,n'} c_n^* c_{n'} E_{n'} \delta_{nn'} \\ &= \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 \\ \Rightarrow \langle H \rangle &\geq E_0 \sum_n |c_n|^2 \\ \Rightarrow \langle H \rangle &\geq E_0 \end{aligned}$$

We can parameterize the wavefunctions in various ways. One way is to include an adjustable parameter in the functional form of the wavefunction itself. For instance, if we consider the Hamiltonian for the harmonic oscillator, i.e. $H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$, and the trial function of the form $\psi_a = e^{-ax^2}$, we get through variation theory:

$$\begin{aligned} \int \psi_a H \psi_a dV &= \int e^{-ax^2} \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right\} e^{-ax^2} dx \\ &= \frac{\hbar^2}{2m} \int e^{-ax^2} (-2axe^{-ax^2} + 4a^2x^2e^{-ax^2}) dx \\ &\quad + \frac{1}{2} k \int x^2 e^{-2ax^2} dx \\ &= -\frac{a\hbar^2}{m} \int xe^{-2ax^2} dx + \left(\frac{2a^2\hbar^2}{m} + \frac{1}{2}k \right) \int x^2 e^{-2ax^2} dx \\ &= 0 + \left(\frac{2a^2\hbar^2}{m} + \frac{1}{2}k \right) \frac{1}{4a} \sqrt{\frac{\pi}{2a}} \\ \int e^{-ax^2} \cdot e^{-ax^2} dx &= \sqrt{\frac{\pi}{2a}} \end{aligned}$$

We thus have

$$E = \frac{\left(\frac{2a^2\hbar^2}{m} + \frac{1}{2}k\right)\frac{1}{4a}\sqrt{\frac{\pi}{2a}}}{\sqrt{\frac{\pi}{2a}}} = \frac{a\hbar^2}{2m} + \frac{k}{8a}$$

Minimizing for a implies $dE/da = 0$:

$$\begin{aligned}\frac{dE}{da} &= \frac{\hbar^2}{2m} - \frac{k}{8a^2} = 0 \\ \Rightarrow a^2 &= \frac{km}{4\hbar^2} \\ \Rightarrow a &= \frac{1}{2}\sqrt{\frac{km}{\hbar^2}}\end{aligned}$$

We thus have for the energy and wavefunction:

$$\begin{aligned}E &= \frac{1}{4}\sqrt{\frac{k}{m}}\hbar + \frac{1}{4}\sqrt{\frac{k}{m}}\hbar = \frac{1}{2}\sqrt{\frac{k}{m}}\hbar \\ \psi_a &= e^{-\frac{1}{2}\sqrt{\frac{km}{\hbar^2}}x^2}\end{aligned}$$

Which are the ground state wavefunction and energy of the harmonic oscillator.

The Radial Wavefunctions

In the previous section we learned about the wavefunctions and energy levels of a particle on a sphere. This model comes very close to the description of an electron circling around a proton nucleus, i.e. the hydrogen atom. However, we have assumed that the potential energy is zero everywhere. This is certainly not true for the hydrogen atom. The electron experiences a potential which is defined by the Coulombic interaction with the nucleus. In this section we focus on taking this potential into account so that we can solve the wavefunctions for the hydrogen atom system.

The Radial Schrödinger Equation

The Coulombic potential energy is:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

The full Hamiltonian of the electron-nucleus system is therefore:

$$\hat{H} = -\frac{\hbar^2}{2m_n}\nabla_{r_n}^2 - \frac{\hbar^2}{2m_e}\nabla_{r_e}^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

In order to solve the Schrödinger equation using this Hamiltonian, we need to consider the following points:

1. Separating the degrees of freedom of the electron from those of the nucleus, so that we are only dealing with electronic wavefunctions.
2. Separating the angular motion from the motion in the radial direction. The Coulombic potential only depends on r and is independent of (θ, ϕ) . This suggests that we might be able to solve the problem considering only the radial coordinate.

The first point is readily achieved by writing the Hamiltonian in terms of the center-of-mass coordinates and the relative distance between the nucleus and the electron. For the kinetic energy part it is found that:

$$\begin{aligned} M &= m_n + m_e, & \frac{1}{\mu} &= \frac{1}{m_n} + \frac{1}{m_e} \\ R &= \frac{m_e r_e + m_n r_n}{M}, & r &= r_n - r_e \\ -\frac{\hbar^2}{2m_n}\nabla_{r_n}^2 - \frac{\hbar^2}{2m_e}\nabla_{r_e}^2 &= -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 \end{aligned}$$

The potential energy contribution is only dependent on relative distance r . We then only solve for the relative distance and ignore the overall translational

motion of the atom in space, in which case the Schrödinger equation becomes:

$$\begin{aligned}
 -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi &= E\psi \\
 \frac{1}{r}\frac{d^2}{dr^2}r\psi + \frac{1}{r^2}\Lambda^2\psi + \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r}\psi &= -\left(\frac{2\mu E}{\hbar^2}\right)\psi
 \end{aligned}$$

To achieve the second point, we will write the wavefunction as $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, where $Y(\theta, \phi)$ are the spherical harmonics that are the solutions in the angular dimension. If we substitute these functions into the Schrödinger equation we get:

$$\begin{aligned}
 \frac{1}{r}\frac{d^2}{dr^2}rRY - \frac{l(l+1)}{r^2}RY + \frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r}RY &= -\left(\frac{2\mu E}{\hbar^2}\right)RY \\
 \frac{1}{r}\frac{d^2(rR)}{dr^2} + \left\{\frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2 r} - \frac{l(l+1)}{r^2}\right\}R &= -\left(\frac{2\mu E}{\hbar^2}\right)R
 \end{aligned}$$

We first multiply this equation with r , and then define the function $\Pi = rR$. We then can write the Schrödinger equation, which depends only on the radial coordinate r , as:

$$\frac{d^2\Pi}{dr^2} - \left(\frac{2\mu}{\hbar^2}\right)V_{eff}\Pi = -\left(\frac{2\mu E}{\hbar^2}\right)\Pi$$

where the effective potential is defined as:

$$V_{eff} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Note the following:

- The angular part has been divided out in the Schrödinger equation. The contribution from the angular dimension is implicitly present in the effective potential through the $l(l+1)\hbar^2$ term.
- The coulombic part provides an attractive (negative) potential. The angular term, however, provides a repulsive (positive) potential. These two effects will counterbalance depending on the quantum number l and the distance from the nucleus r .
- The angular centrifugal force is zero for $l = 0$. This implies that the potential is purely attractive and thus that there is a finite chance of finding the electron at the nucleus.
- Close to the nucleus, the angular centrifugal force for $l \neq 0$ is larger than the attractive coulombic force. Consequently, the electron is expelled from the nucleus and the probability of finding the electron at the nucleus is zero.

The Radial Wavefunctions

Solving the radial Schrödinger equation is nontrivial and we therefore rely on specific mathematical tricks for finding the wavefunctions. Fortunately, the outcome to this differential equation is well-known. The wavefunctions take on the form of *associated Laguerre functions* multiplied by a decaying exponential. The radial functions $R_{n,l}$ are labeled by two quantum numbers: the principal quantum number $n = 1, 2, \dots$ and the momentum quantum number $l = 0, 1, \dots, (n - 1)$:

$$R_{nl}(r) = - \left\{ \left(\frac{2Z}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\} \rho^l L_{n+l}^{2l+1} e^{-\rho/2}$$

where the associated Laguerre function L_n^k is a polynomial given by:

$$L_n^k(x) = \frac{e^x x^{-k}}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+k}) = (-1)^k \frac{d^k}{dx^k} [L_{n+k}(x)]$$

We now define:

$$\rho = \left(\frac{2Z}{na} \right) r, \quad a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

Then the first few radial wavefunctions $R_{n,l}$ are given by:

n	l	$R_{n,l}(\rho)$
1	0 (1s)	$\left(\frac{Z}{a}\right)^{3/2} 2e^{-\rho/2}$
2	0 (2s)	$\left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{2}}(2 - \rho)e^{-\rho/2}$
2	1 (2p)	$\left(\frac{Z}{a}\right)^{3/2} \frac{1}{2\sqrt{6}}\rho e^{-\rho/2}$

Note the following:

- The radial wavefunction has zero amplitude at the nucleus for $l \neq 0$ and nonzero amplitude for $l = 0$
- The number of nodes is $n - l - 1$

Energy Levels

The total hydrogenic wavefunction is:

$$\Psi_{n,l,m_l} = R_{n,l,m_l} Y_{l,m_l}$$

The quantum numbers are:

$$\begin{aligned} n &= 1, 2, \dots \\ l &= 0, 1, 2, \dots, n-1 \quad (n) \text{ levels} \\ m_l &= 0, \pm 1, \pm 2, \dots, \pm l \quad (2l+1) \text{ levels} \end{aligned}$$

The energies are:

$$E_n = - \left(\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \right) \frac{1}{n^2}$$

Each of these n -levels has n different l states, which in turn have $2l + 1$ different m_l states. Note the following:

- The energy only depends on the principal quantum number n . The quantum number for the momentum l does not influence the energy.
- Each level n has $(n - 1)$ sub-levels of the same energy with $l = 0, 1, \dots, n - 1$
- The total number of levels for a given level labeled with l , is $2l + 1$, which results from the possible allowed values of the quantum number m_l .
- The energy level spacing decreases quadratically.

The total degeneracy for each level n is:

$$g = \sum_{l=0}^{n-1} 2l + 1 = n^2$$

We can visualize the levels schematically as:

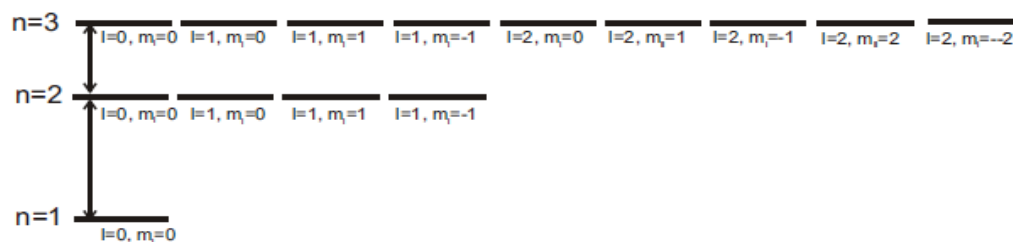


Figure 1: energy diagram

The Hydrogen Atomic Orbitals

We are now in a position to construct the atomic orbitals of the hydrogen atom. We will look at their energies, degeneracies and probability distribution in space.

The Probability Distribution

The Hydrogen wavefunctions are normalized over whole space, i.e. the chance of finding the electron wavefunction somewhere must be 1. The normalization condition is:

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi \Psi_{n,l,m_l}^* \Psi_{n',l',m_l'}^* dV = \delta_{n,n'} \delta_{l,l'} \delta_{m_l,m_l'}$$

where the incremental volume element is defined as:

$$dV = r^2 \sin \theta dr d\theta d\phi$$

The probability density of finding the electron in volume element $dV = r^2 \sin \theta d\theta d\phi dr$ is:

$$|\Psi_{n,l,m_l}|^2 dV$$

What is the probability of finding the electron between the distance r and $r + dr$ from the nucleus? We find this by integrating out the angular part as follows:

$$\begin{aligned} P(r)dr &= \int_\Omega |\Psi_{n,l,m_l}|^2 dV = \int_0^\pi \int_0^{2\pi} R^2 |Y|^2 r^2 \sin \theta dr d\theta d\phi \\ &= R^2 r^2 dr \int_0^\pi \int_0^{2\pi} |Y|^2 \sin \theta d\theta d\phi \\ &= R^2 r^2 dr \end{aligned}$$

We call $P(r) = R^2 r^2$ the radial distribution function. The r^2 takes care of the fact that a surface at distance r from the nucleus expands like r^2 . Hence, for larger r , we are dealing with a larger segment of space, which in turn increases the chance of finding the electron there. Without the r^2 we are not considering the true three-dimensional geometry of the problem.

The most probable distance to find the electron at is obtained by finding r for which $dP/dr = 0$. For the wavefunction $\Psi_{1,0,0}$ this is:

$$\begin{aligned} \frac{dP}{dr} &= \frac{d}{dr} R_{1,0,0}^2 r^2 = 4 \left(\frac{Z}{a} \right)^3 \frac{d}{dr} r^2 e^{-2Zr/a} \\ &= 4 \left(\frac{Z}{a} \right)^3 (2 - 2Zr/a) r e^{-2Zr/a} = 0 \\ &\rightarrow r_{max} = a/Z \end{aligned}$$

with

$$a = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \approx \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = a_0 = 0.529 \text{ \AA}$$

where a_0 is known as the Bohr radius.

Mean Radius

The mean radius is defined as the expectation value of r , not to be confused with the most probable radius (found through $d(R_{nl}^2 r^2)/dr = 0$). We can calculate the mean radius as:

$$\begin{aligned} \langle r \rangle &= \int_V \Psi_{n,l,m_l}^* r \Psi_{n,l,m_l} dV = \int_0^\infty R_{nl}^* r R_{nl} r^2 dr \int_0^{2\pi} \int_0^\pi Y_{l,m_l}^* Y_{l,m_l} \sin \theta d\theta d\phi \\ &= \int_0^\infty R_{nl}^* r R_{nl} r^2 dr = \left(\frac{2Z}{na} \right)^2 \left[\frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^2 \int_0^\infty e^{-\rho} \rho^{2l+3} [L_{n+l}^{2l+1}(\rho)]^2 d\rho \end{aligned}$$

This integral can be solved using standard Laguerre identities (see <http://mathworld.wolfram.com/LaguerrePolynomial.html>). The outcome of this integral is:

$$\langle r \rangle = \frac{n^2 a_0}{Z} \left\{ \frac{3}{2} - \frac{l(l+1)}{2n^2} \right\}$$

Note that the mean radius of an s-orbital is greater than that of a p-orbital for the same principal quantum number (shell), due to the presence of an additional node in the s-orbital ($n-1$ for s, $n-2$ for p-orbitals).

s-Orbitals

s-Orbitals have zero angular momentum and thus $l = 0$ and $m_l = 0$. The first two levels (1s) and (2s) are given as:

$$\begin{aligned} \Psi_{n,l,m_l} &= R_{n,l,m_l} Y_{l,m_l} \quad l = 0, \quad m_l = 0 \\ \Psi_{1,0,0} &= R_{1,0,0} \left(\frac{1}{2\pi} \right)^{1/2} = \left(\frac{1}{2\pi} \right)^{1/2} \left(\frac{Z}{a} \right)^{3/2} 2e^{-Zr/a} \\ \Psi_{2,0,0} &= R_{2,0,0} \left(\frac{1}{2\pi} \right)^{1/2} = \left(\frac{1}{2\pi} \right)^{1/2} \left(\frac{Z}{a} \right)^{3/2} \frac{1}{2\sqrt{2}} (2 - Zr/a) e^{-Zr/2a} \end{aligned}$$

Note that:

- Because s-orbitals have no angular dependence, they are spherically symmetric.
- There is a finite chance to find the electron at the nucleus. This chance, however, has to be put in the proper perspective by realizing that at the nucleus the wavefunction has maximum curvature and thus maximum kinetic energy. The electron will therefore 'shoot through' the nucleus instead of sitting permanently at the origin.

p-Orbitals

p-Orbitals are orbitals with $l = 1$. For every n there are 3 p-levels, labeled with $m_l = 0, m_l = 1, m_l = -1$. These three levels are given by:

$$\begin{aligned} p_z &= \left(\frac{3}{4\pi}\right)^{1/2} R_{n,l}(r) \cos \theta \\ p_+ &= -\left(\frac{3}{8\pi}\right)^{1/2} R_{n,l}(r) \sin \theta e^{i\phi} \\ p_- &= \left(\frac{3}{8\pi}\right)^{1/2} R_{n,l}(r) \sin \theta e^{-i\phi} \end{aligned}$$

It is more custom to combine the last two orbitals and rewrite them as real and imaginary parts. These new combined orbitals align with the x - and y -axis and are therefore easier to visualize. They are given by:

$$\begin{aligned} p_x &= \frac{1}{\sqrt{2}}(p_- - p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n,l}(r) \sin \theta \cos \phi \\ p_y &= \frac{i}{\sqrt{2}}(p_- + p_+) = \left(\frac{3}{4\pi}\right)^{1/2} R_{n,l}(r) \sin \theta \sin \phi \end{aligned}$$

If we now remember that $x = r \sin \theta \cos \phi$ and that $y = r \sin \theta \sin \phi$, we see that the p_x orbital has 'x'-character and the p_y orbital has 'y'-character. Indeed, these composite orbitals are aligned along the respective axes. Note also that:

- Because of the nonzero angular momentum, p-orbitals have a zero radial probability distribution at the origin.
- The p_x and p_y functions are also valid wavefunctions. In general, for degenerate states, we can write a linear combination of eigenstates $\psi = A|n\rangle + B|m\rangle$ as a new solution of the Schrödinger equation. The p_x and p_y function fulfill this condition. Note that this only holds for degenerate states!

d-Orbitals

d-Orbitals have angular momentum $l = 2$ and thus occur for levels with $n \geq 3$. There are 5 d-orbitals for every quantum number $n \geq 3$. It is custom to compose linear combinations of these five solutions to end up with wavefunctions with intuitive symmetries:

$$\begin{aligned} d_{z^2} &= d_0 = \left(\frac{5}{16\pi}\right)^{1/2} R_{n2}(r)(3z^2 - r^2)/r^2 \\ d_{x^2-y^2} &= \frac{1}{\sqrt{2}}(d_{+2} + d_{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} R_{n2}(r)(x^2 - y^2)/r^2 \end{aligned}$$

$$d_{xy} = \frac{1}{i\sqrt{2}}(d_{+2} - d_{-2}) = \left(\frac{15}{4\pi}\right)^{1/2} R_{n2}(r)xy/r^2$$

$$d_{yz} = \frac{1}{i\sqrt{2}}(d_{+1} + d_{-1}) = -\left(\frac{15}{4\pi}\right)^{1/2} R_{n2}(r)yz/r^2$$

$$d_{zx} = \frac{1}{\sqrt{2}}(d_{+1} - d_{-1}) = -\left(\frac{15}{4\pi}\right)^{1/2} R_{n2}(r)zx/r^2$$

Textbook

1. A.K.Chandra, 2010, Introductory quantum Chemistry, Tata McGraw Hill Education Pvt., Ltd, New Delhi
2. Puri Sharma and Pathania, 2013, Elements of Physical Chemistry, Vishal Publishing Co., New Delhi

Possible Questions

PART- A Questions

(Each Question carries one mark)

1. Evidence in favour of the wave nature of radiation
 - a. **Interference of radiation**
 - b. Photoelectric effect
 - c. Compton effect
 - d. Black body radiation
2. Black body radiation has a characteristic
 - a. **Continuous spectrum**
 - b. Discontinuous spectrum
 - c. Narrow range of light
 - d. Laser action
3. As per plancks law the characteristic continuous spectrum of radiation depends upon
 - a. **Body's temperature**
 - b. Nature of the body
 - c. Colour of the body
 - d. Density of the body
4. Stefan Boltzmann law is based on
 - a. Diffraction of radiation
 - b. Photoelectric effect
 - c. Compton effect
 - d. **Black body radiation**
5. In one dimensional box problem the potential energy of the particle outside the box is
 - a. zero
 - b. unity
 - c. **infinity**
 - d. fractional
6. The energy levels of the particle in the box are
 - a. quantized
 - b. randomized
 - c. dispersed
 - d. Not-quantised
7. The theory of rigid rotor in space is useful in dealing with
 - a. **Rotational spectra of diatomic molecules**
 - b. Vibrational spectra of diatomic molecules
 - c. IR spectra of diatomic molecules
 - d. Raman spectra of diatomic molecules

8. In the Hook's law $f = -kx$, k is called
 - a. **Force constant**
 - b. Gas constant
 - c. Boltzmann constant
 - d. Faraday's constant
9. The lowest energy orbital for the ammonia molecule is designated
 - a. $1s$
 - b. $1\sigma_g$
 - c. **$1a_1$**
 - d. C_{3v}
10. The benzene molecule C_6H_6 has how many vibrational modes
 - a. 6
 - b. 12
 - c. 24
 - d. **30**
11. Zeeman effect is
 - a. **the change in energy levels of an atom when it is placed in uniform external field**
 - b. The change in energy levels of an atom when placed in non-uniform external field
 - c. The change in energy levels of an atom when placed in external electric field
 - d. The change in energy levels of an atom when placed in non-uniform electric field
12. The energy level belongs to $E_n = 2n - 1/2$
 - a. **Harmonic oscillator**
 - b. Hydrogen atom
 - c. particle in a box
 - d. free particle in motion
13. The shape of $BeCl_2$ molecules is
 - a. **Linear**
 - b. Triangular planar
 - c. Tetrahedral
 - d. octahedral
14. Example for tetrahedral molecule
 - a. $BeCl_2$
 - b. boron trifluoride
 - c. **methane**
 - d. phosphorous pentachloride
15. If the symmetry element is the 'plane of symmetry' then the corresponding symmetry operation is
 - a. Doing nothing
 - b. **reflection**
 - c. Inversion of all coordinates
 - d. Rotation through an angle of $360/n$ about an axis where 'n' is the order of the axis
16. For the symmetry operation "rotation" the corresponding symmetry element is
 - a. Identity element
 - b. Plane of symmetry
 - c. Centre of symmetry
 - d. **Proper axis of symmetry**
17. For a pyramidal molecule with point group C_{3v} the number of theoretically predicted IR fundamental bands
 - a. **Three**
 - b. Four
 - c. Five
 - d. Six
18. For chloro trifluoride molecule the number of observed Raman bands and IR bands are four each, the predicted geometry is
 - a. Pyramidal
 - b. planar
 - c. **T-shaped**
 - d. bent
19. In case of molecules with a centre of symmetry the vibrational modes are anti-symmetric to centre of inversion are
 - a. IR inactive
 - b. **IR active**
 - c. Raman inactive
 - d. Raman hyper active
20. For Raman activity the vibrations should involve a change in
 - a. **polarizability**
 - b. magnetization
 - c. Magnetic susceptibility
 - d. Surface tension

PART- B Questions

(Each questions carries six marks)

21. (a). Derive time independent Schrodinger wave equation.

(OR)

- (b). Define photoelectric effect. How quantum theory explains photoelectric effect?

Approximation and Variation Methods (2017 Batch)

22. (a). Discuss the illustration of uncertainty principle and correspondence principle with reference to harmonic oscillator.
(OR)
(b). Derive the solution of Schrodinger wave equation for one dimensional harmonic oscillator.
23. a. Explain the most probable distance of the hydrogen atom -1s electron.
(OR)
b. Explain variation method to obtain approximate solution to a wave equation.
24. (a). (i) Write notes on the meaning of improper rotation.
(ii) Define inversion operation? Is it equivalent to any other combination of operations. Give an example.
(OR)
(b) (i) What are the different types of groups? Explain with example.
(ii) Distinguish between point group and space group.
25. (a). (i) Construct the C_{2v} character table.
(ii) State and explain the great orthogonality theorem.
(OR)
(b). (i) Define reducible and irreducible representation.
(ii) What are the relationships between reducible and irreducible representation of the group.

PART- C Question

(Each question carries ten marks)

26. Solve the Schrodinger wave equation for a particle in three dimensional box for its energy and show that the energy states are orthogonal



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 (Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
 (For the candidates admitted from 2017 & onwards)
Quantum Chemistry

Multiple Choice Questions for Unit III

S. NO	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	In Perturbation method	a system which wave functions may be guessed	method to obtain approximate solutions to the wave equation	method to obtain accurate solutions to the wave equation	a system which wave functions is accurately known	method to obtain approximate solutions to the wave equation
2	In variation method	a system which wave functions may be guessed	method to obtain approximate solutions to the wave equation	method to obtain accurate solutions to the wave equation	a system which wave functions is accurately known	a system which wave functions may be guessed
3	In this method a trial wave function ought to be close to the true wave function of the system concerned and the mean energy is then calculated	Perturbation method	Variation method	Normalization of the wave function	Making the wave functions orthogonal	Variation method

4	The method applicable for a system which wave functions may be guessed	Perturbation method	Variation method	Normalization of the wave function	Making the wave functions orthogonal	Variation method
5	The method applicable for a system which differs in a very small way from one for which the exact solution is known	Perturbation method	Variation method	Normalization of the wave function	Making the wave functions orthogonal	Perturbation method
6	The method to obtain approximate solutions to the wave equation	Variation method	Normalization of the wave function	Making the wave functions orthogonal	Making the wave functions orthonormal	Variation method
7	The method to obtain approximate solutions to the wave equation	Perturbation method	Normalization of the wave function	Making the wave functions orthogonal	Making the wave functions orthonormal	Perturbation method
8	An one electron system whose potential field is not spherically symmetrical	Hydrogen atom	Hydrogen atom in magnetic field	Hydrogen molecule	Helium molecule	Hydrogen atom in magnetic field
9	An one electron system whose potential field is not spherically symmetrical	Hydrogen atom	Hydrogen atom in electric field	Hydrogen molecule	Helium molecule	Hydrogen atom in electric field
10	The sum of the energies of the third and the fourth level is	$10 \pi^2 h^2 / mL^2$	$10 \pi^2 h^2 / 3 mL^2$	$11 h^2 \pi^2 / mL^2$	$11 h^2 \pi^2 / mL^2$	$10 \pi^2 h^2 / mL^2$
11	The ratio of the reflected to the incident amplitude A_R/A_0	$1 - A_T/A_0$	$\sqrt{1-T}$ in magnitude	a real negative number	$1 + A_T/A_0$	$1 - A_T/A_0$
12	The expected value of kinetic energy in terms of h, k and m is	$\hat{E}_k = h^2/2m$	$\hat{E}_k = h^2 k^2 / m$	$\hat{E}_k = h^2 k^2 / 2m$	$\hat{E}_k = h^2 k^2 / 2m$	$\hat{E}_k = h^2 k^2 / 2m$
13	Time relation between Ψ and E_k is	$\hat{E}_k \Psi = h^2/2m \Psi$	$\hat{E}_k \Psi = h^2 k^2 / 2m \Psi$	$\hat{E}_k \Psi = h^2 k^2 / m \Psi$	$\hat{E}_k \Psi = h^2 k^2 / m^2 \Psi$	$\hat{E}_k \Psi = h^2 k^2 / 2m \Psi$

14	Which of the following are eigen functions of \hat{A}^2 ?	Ψ_1 and Ψ_2	Ψ_2 and not Ψ_1	Ψ_1 and not Ψ_2	Neither Ψ_1 and Ψ_2	Ψ_1 and Ψ_2
15	The expectation value of A for the state $\Psi = (\sqrt{3}\Psi_1 + \sqrt{4}\Psi_2)/5$ is	-0.32	zero	0.75	0.96	0.96
16	Throughout $0 < x < L$, the wave function	Can be chosen to be real	is exponentially decaying	is generally complex	is zero	Can be chosen to be real
17	probability of least probable isotopomer is	$(0.00015)^2 \times 0.011$	$(0.00015)^2 \times 0.989$	$(0.99985)^2 \times 0.011$	$0.99985 \times 0.00015 \times 0.989$	$(0.00015)^2 \times 0.011$
18	Least probable isotopomer is	D- ^{13}C -D	^1H - ^{13}C - ^1H	D- ^{12}C -D	D- ^{12}C -H	D- ^{13}C -D
19	Total number of isotopomers of ethylene diradical are	4	6	8	10	6
20	The value of using variation method is :	$a \geq 1$	$a = 0$	$a = 0$ to 1	$a = -1$ to $+1$	$a = 0$
21	Value of $\langle H \rangle$ is	greater than E_0	greater than and equal to E_0	less than E_0	Less than and equal to E_0	greater than and equal to E_0
22	The second order correction to E_1 is	zero	A	$A^2/E_2 - E_1$	$A^2/E_1 - E_2$	$A^2/E_2 - E_1$
23	The first order correction to E_1 is	4 A	2 A	A	Zero	A
24	The degeneracy of the fourth level is given by	1	2	3	4	4
25	The energy level belongs to $E_n \propto n^2$	Harmonic oscillator	Hydrogen atom	particle in a box	free particle in motion	Hydrogen atom
26	The energy level belongs to E_n is continuous	Harmonic oscillator	Hydrogen atom	particle in a box	free particle in motion	free particle in motion
27	The energy level belongs to $E_n = n^2$	Harmonic oscillator	Hydrogen atom	particle in a box	free particle in motion	particle in a box

28	The energy level belongs to $E_n=2n-1/2$	Harmonic oscillator	Hydrogen atom	particle in a box	free particle in motion	Harmonic oscillator
29	Write the energy level for the free particle in motion	$E_n=2n-1/2$	$E_n=n^2$	E_n is continuous	$E_n \propto n^2$	E_n is continuous
30	Write the energy level for the particle in a box	$E_n=2n-1/2$	$E_n=n^2$	E_n is continuous	$E_n \propto n^2$	$E_n=n^2$
31	Write the energy level for the Hydrogen atom	$E_n=2n-1/2$	E_n is continuous	$E_n=n^2$	$E_n \propto n^2$	$E_n \propto n^2$
32	Write the energy level for the Harmonic oscillator system	$E_n=2n-1/2$	$E_n=n^2$	E_n is continuous	$E_n \propto n^2$	$E_n=2n-1/2$
33	The first order perturbed Hamiltonian, when an external uniform electric field E is applied to the z -axis on an atom is	$H'=Eez$	$H'=-Eez$	$H'=Ez/e$	$H'=-Ez/E$	$H'=-Eez$
34	When a perturbation of cx^3 is applied in the Hamiltonian of harmonic oscillation, the shift in first order energy is	zero	$3/4 \, c(\hbar\omega/k)^2$	$1/2 \, c(\hbar\omega/k)^2$	$C \, \hbar\omega/k$	Zero
35	Zeeman effect is	the change in energy levels of an atom when it is placed in uniform external field	The change in energy levels of an atom when placed in non-uniform external field	The change in energy levels of an atom when placed in external electric field	The change in energy levels of an atom when placed in non-uniform electric field	the change in energy levels of an atom when it is placed in uniform external field

36	A one dimensional harmonic oscillator of mass m, charge q and classical amplitude a is kept in an electric field strength E along x. First order change in ground and first excited state are respectively	$0, qEa/2$	$0, qEa$	$0, 0$	$qEa/\alpha, qEa$	$qEa/\alpha, qEa$
37	In the first order correction to eigen function $[1\&0]$ is	$[0\&A^*/E_1 - E_2]$	$[0\&1]$	$[A^*/E_1 - E_2\&0]$	$[1\&1]$	$[A^*/E_1 - E_2\&0]$
38	In the above question, the second order correction to E_1 is	0	A	$A^2/E_2 - E_1$	$A^2/E_1 - E_2$	$A^2/E_2 - E_1$
39	An unperturbed two level system has energy eigen values E_1 and E_2 and eigen functions $[1\&0]$ and $[0\&1]$ when perturbed its Hamiltonian is represented by the first order correction to E_1 is	4A	2A	A	Zero	A
40	In case of H- atom the total degeneracy of the state of specified m is given by	$N=n(2L+1)$	$N=n^2$	$N=l(l+1)$	$N=2L+1$	$N=n(2L+1)$
41	A system is known to be in a state by the wave function $\Psi(\theta, \phi) = 1/\sqrt{20} [3Y_{02} + \sqrt{7}Y_{02} - 2Y_{12}]$, the probability of finding the system in a state with $m=0$ is	4/5	1/5	2/5	3/5	04-May
42	The average value of P_x for the box normalized wave function $\Psi(x) = \sqrt{2}/L \sin(3\pi x/L)$	$18\pi^2/L$	$6\pi/L - 1$	0	$18\pi^2$	0
43	If $\Psi = \sqrt{2}/L \cos \pi x/L e^{-Et/\hbar}$, then $\langle x \rangle$ in the limit $-L/2 < x < L/2$ is	$3/4L$	0	$1/4L$	$L/2$	0

44	A particle of mass m is confined to a one dimensional box extending from $x=0$ to $x=a$. Assuming the particle in the first excited state, what is the position-probability density at $x=a/8$?	$1/a$	$2/a$	$1/2a$	$1/4a$	$1/a$
45	A particle with energy $v_0/2$ coming from left encounters a potential $-3v_0/2$ at $x=0$. $V(x)=0$ for $x<a$ and $V(x)=-3v_0/2$ for $x>a$, transmission coefficient is	$1/2$	$2/3$	$4/9$	$8/9$	04-Sep
46	Consider a particle in one dimensional box between $x=0$ and $x=a$. $V(x) = \begin{cases} \infty & \text{for } x<0 \\ 0 & \text{for } 0<x<a \\ \infty & \text{for } x>a \end{cases}$ when is the probability that it will be found in the region $a/4 < x < 3a/4$?	$1/2$	$1/2 + 1/\pi$	$1/4 + 2/\pi$	$1/4 + 1/\pi$	$1/2$
47	A particle is described by a wavefunction $\Psi(x) = e^{-x}$ in one dimension. What is the probability that it will be found in the region $(x)<a, a>0$?	e^{-a}	e^{-2a}	$1 - e^{-a}$	$1 - e^{-2a}$	$1 - e^{-2a}$
48	Consider 8 electrons in a one dimensional box of length a extending from $x=0$ to $x=a$. What is the minimum allowed total energy using Pauli's exclusion principle for the system? (m =mass of electron)	$10h^2/ma^2$	$8h^2/ma^2$	$15h^2/4ma^2$	$15h^2/2ma^2$	$15h^2/4ma^2$
49	what is the fraction of beam reflected from the step barrier of V_0 if energy of electron E with $E > V_0$ and width of barrier is infinite, is given by	E/V_0	$E - V_0/V_0$	$E - V_0/2V_0$	$E + V_0/E$	$E - V_0/V_0$

50	In the electronic transition pictured below, the molecule starts in its ground vibrational level. The most probable vibrational quantum number of the excited state is	1	3	5	4	4
51	Which of the following is a true statement about the fluorescence of a molecule whose ground state is a singlet:	Its dissociation must proceed by a unimolecular mechanism.	The excited state must be a triplet	The excited state must have the same geometry as the ground state.	Fluorescence can occur in the visible region after absorption in the ultraviolet.	Fluorescence can occur in the visible region after absorption in the ultraviolet.
52	The benzene molecule C ₆ H ₆ has how many vibrational modes	6	12	24	30	30
53	The lowest energy orbital for the ammonia molecule is designated	1s	1σ _g	1a ₁	C _{3v}	1a ₁
54	The force constant in NO equals	1125	1342	1240	1595	1595
55	The equilibrium internuclear distance in NO equals	115	121	140	171	115
56	For NO, the J → 0 to J → 1 transition occurs at	1.705	3.41	121	8.628	3.41
57	The spectroscopic constants assigned for the NO molecule are	D ₀ = 6.48eV	D ₀ = 7.48eV	D ₀ = 8.48eV	D ₀ = 9.48eV	D ₀ = 6.48eV
58	A certain symmetry group of order 8 has 5 irreducible representations. What is the highest possible degeneracy of its quantum states	1	2	3	5	2
59	Example for a low symmetry point group	C ₁	D ₂	C _{2h}	S ₄	C _s

60	Zeeman effect is	the change in energy levels of an atom when it is placed in uniform external field	The change in energy levels of an atom when placed in non-uniform external field	The change in energy levels of an atom when placed in external electric field	The change in energy levels of an atom when placed in non-uniform electric field	the change in energy levels of an atom when it is placed in uniform external field
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UNIT – IV

Fundamental of Group Theory

Symmetry elements and symmetry operations - definition of identical and equivalent elements configurations - effect of performing successive operations commutative and non-commutative - inverse operations.

Groups and their basic properties - definition of a group - basic properties of a group-definition of abelian - cyclic- isomorphic, finite, infinite groups and subgroup. Symmetry classification of molecules into point groups-Schoenflies symbol (only-difference between point group and space group).

Matrices- Definition of matrix, square matrix, diagonal matrix, null matrix, unit matrix, row matrix, column matrix, symmetric matrix, skew symmetric matrix and conjugate matrix. Multiplication, commutative and non commutative-determination of inverse of a matrix, block multiplication of matrices-addition and subtraction of matrices.

Matrix notations for symmetry operations of C_{2v} and C_{3v} groups-construction of character tables for C_{2v} and C_{3v} point groups.

Symmetry Elements and Symmetry Operations

A symmetry element is a geometric entity (point, line or plane). A symmetry operator performs an action on a three dimensional object. Symmetry operators are similar to other mathematical operators.

We will use only five types of operators in this subject

Operator	Symbol
Identity	E
Rotation	C
Mirror plane	σ
Inversion	i
Improper rotation	S

All symmetry operators leave the shape (molecule) in an equivalent position, i.e. it is indistinguishable before and after the operator has performed its action.

Identity (E)

This operator does nothing and is required for completeness. Equivalent to multiplying by 1 or adding 0 in algebra.

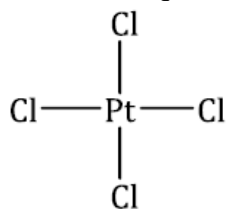
Rotation (C)

Rotate clockwise around an axis by $2\pi/n$ if the rotation brings the shape (molecule) into an equivalent position.

The symmetry element is called the axis of symmetry. For a $2\pi/n$ rotation there is an n-fold axis of symmetry. This is denoted as C_n .

Many molecules have more than one symmetry axis. The axis with the largest 'n' is called the principal axis.

Consider a square planar molecule like $PtCl_4$.



C_4 C_4^2 C_4^3 C_4^4 possible rotations. $C_4^2 \rightarrow C_2$ and $C_4^4 \rightarrow E$

We classify this as E , $2C_4$, C_2 . There are also two other C_2 axes (along the bonds and between the bonds)

Reflection (σ)

The shape (molecule) is reflected through a plane. (spiegel is German for "mirror")

If a plane is \perp to the principal rotation axis then it is called σ_h (horizontal). If it is along the principal axis then it is called σ_v (vertical). There may be more than one σ_v . If the plane bisects an angle between 3 atoms then it is called σ_d (dihedral). The reflection plane is the symmetry element.

Inversion (i)

All points in the shape (molecule) are reflected through a single point. The point is the symmetry element for inversion. This turns the molecule inside out in a sense. The symmetry element is the point through which the shape is inverted.

Improper Rotation (S)

Rotation by $2\pi/n$ followed by reflection, σ perpendicular to the rotation axis. Since performing σ two times is the same as doing nothing (E), S can only be performed an odd number of times.

$$S_n^k = \sigma_h C_n^k \quad \text{if } k \text{ is odd}$$

$$S_n^k = C_n^k \quad \text{if } k \text{ is even}$$

k must be an odd value

$$\text{e.g. } S_3^2 = C_3^2 \text{ and } S_3^5 = \sigma_h C_3^5$$

Additionally...

$$S_1 = \sigma_h$$

$$S_n^n = \sigma_h \quad \text{if } n \text{ is odd}$$

$$S_n^n = E \quad \text{if } n \text{ is even}$$

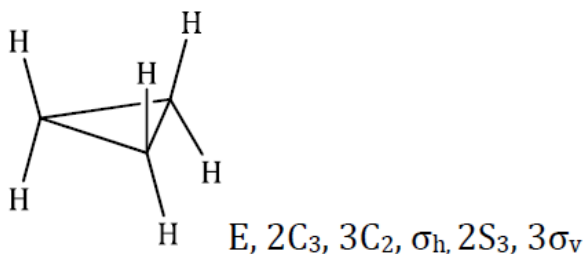
The symmetry element for S is the rotation axis.

Symmetry Operations

Identifying all symmetry elements and operations in molecules.

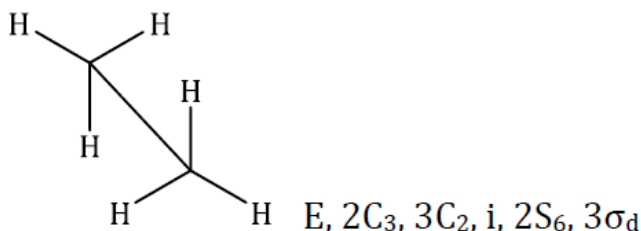
Cyclopropane – D_{3h}

Cyclopropane – D_{3h}



There is an S_3^1 and an S_3^5 (also called S_3^{-1})

Ethane (staggered) – D_{3d}



Definition of a Group

There are four defining rules for groups.

1. The combination of any two elements as well as the square of each element must be in the group.

Combining rule can be defined as anything (multiplication, differentiation, one followed by another, etc...)

$PQ = R$; R must be in the group

The commutative law may not hold $AB \neq BA$

2. One element must commute with all other elements and leave them unchanged. That is, an identity element must be present.

$ER = RE = R$; E must be in the group

3. The associative law must hold.

$P(QR) = (PQ)R$; for all elements

4. Every element must have an inverse which is also in the group.

$RR^{-1} = R^{-1}R = E$; R^{-1} must be in the group

Summary

Definition of a group

$PQ = R$ R must be in the group

$ER = RE = R$ E must be in the group

$P(QR) = (PQ)R$ for all elements

$$RR^{-1} = R^{-1}R = E \quad R^{-1} \text{ must be in the group}$$

Example Groups

With a combining rule of addition, all integers form a group.

The identity element is 0, and the inverse of each element is the negative value.

This is an example of an infinite group.

With a combining rule of multiplication, we can form a finite group with the following set $\{i, -i, 1, -1\}$. The identity element is 1 in this case.

A set of matrices can also form a finite group with the combining rule of matrix multiplication.

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

The identity matrix is $\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$

e.g.

$$\begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

$$\sum_k^n A_{ik} \times B_{kj} = (AB)_{ij}$$

A_{ik} = element in the i^{th} row and k^{th} column

Lastly, the set of symmetry operators (not symmetry elements) present for a given molecular shape forms a group with the combining rule of one followed by another.

These types of groups are called point groups.

Group Multiplication Tables

The number of elements in the group is called the order of the group (h)

Rearrangement Theorem:

In a group multiplication table, each row and column lists each element in the group once and only once. No two rows or two columns may be identical.

Consider a group of order 3

G_3	E	A	B
E	E	A	B
A	A	?	?
B	B	?	?

There are two options for filling out the table $AA = B$ or $AA = E$
 If $AA = E$ then the table becomes...

G_3	E	A	B
E	E	A	B
A	A	E	B
B	B	A	E

This violates the rearrangement theorem as the last two columns have elements that appear more than once.

The only solution for group G_3 is

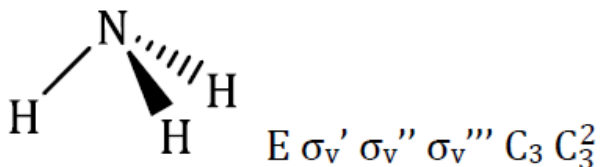
G_3	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

Note: The group G_3 is a member of a set of groups called cyclic groups. Cyclic groups have the property of being Abelian, that is all elements commute with each other.

A cyclic group is one which every element can be generated by a single element and its powers. In this case $A = A$ and $AA = A^2 = B$ and $AAA = A^3 = E$.

Point Groups

Consider all of the symmetry operations in NH_3



NH ₃	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
E	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
σ_v'	σ_v'	E	C_3	C_3^2	σ_v''	σ_v'''
σ_v''	σ_v''	C_3^2	E	C_3	σ_v'''	σ_v'
C_3	σ_v'''	C_3	C_3^2	E	σ_v'	σ_v''
C_3^2	C_3	σ_v'''	σ_v'	σ_v''	C_3^2	E
C_3^2	C_3^2	σ_v''	σ_v'''	σ_v'	E	C_3

Note that all of the rules of a group are obeyed for the set of allowed symmetry operations in NH₃.

G ₆	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Compare the multiplication table of NH₃ to that of G₆.

There is a 1:1 correspondence between the elements in each group

$$E \rightarrow E$$

$$\sigma_v' \rightarrow A$$

$$\sigma_v'' \rightarrow B$$

$$\sigma_v''' \rightarrow C$$

$$C_3 \rightarrow D$$

$$C_3^2 \rightarrow F$$

Groups that have a 1:1 correspondence are said to be isomorphic to each other.

If there is a more than 1:1 correspondence between two groups, they are said to be homomorphic to each other. All groups are homomorphic with the group E. i.e. $A \rightarrow E$, $B \rightarrow E$, $C \rightarrow E$ etc...

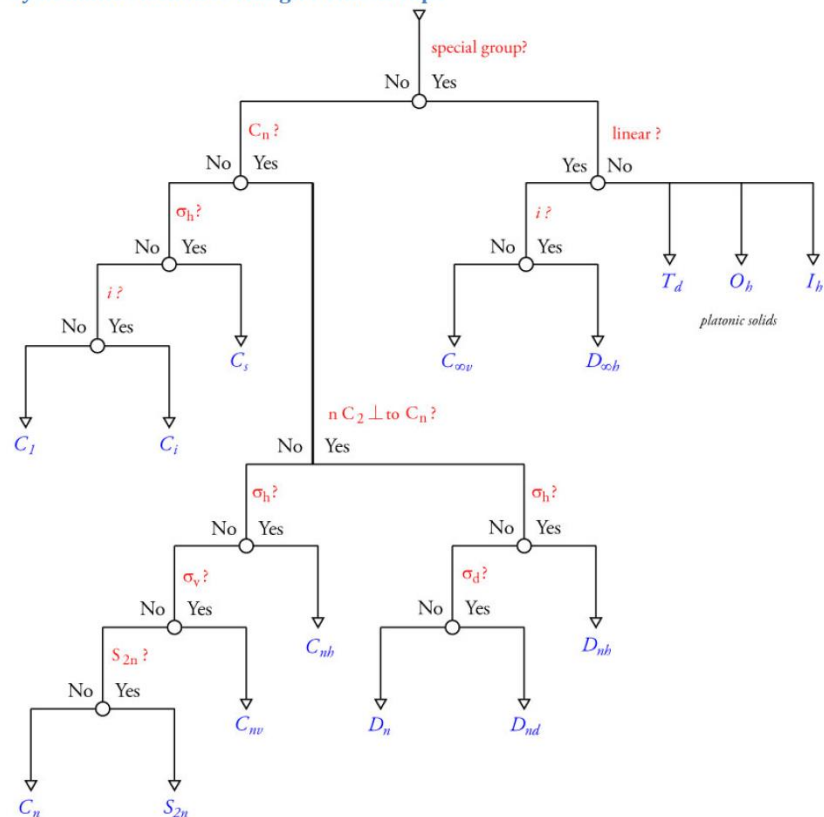
Classification of point groups

Schoenflies Notation

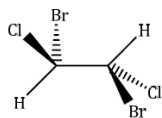
Group Name	Essential Symmetry Elements*	
C_s	one σ	
C_i	one i	
C_n	one C_n	
D_n	one C_n plus $nC_2 \perp$ to C_n	
C_{nv}	one C_n plus $n\sigma_v$	
C_{nh}	one C_n plus σ_h	
D_{nh}	those of D_n plus σ_h	
D_{nd}	those of D_n plus σ_d	
S_n (even n)	one S_n	
T_d	tetrahedron	Special Groups
O_h	octahedron	
I_h	icosahedrons	
H_h	sphere	

Systematic classification of a group

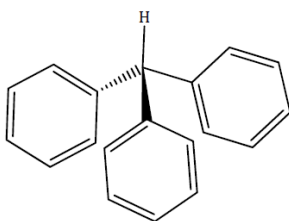
Systematic Method to Assign Point Groups



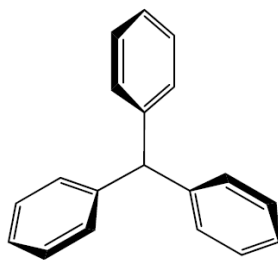
Assign the point groups to the following molecules



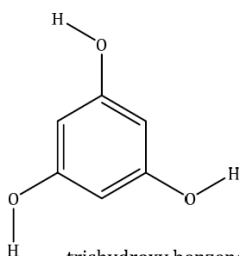
dichlorodibromo ethane i only $\rightarrow C_i$



triphenyl methane

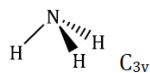


$C_n \rightarrow C_3$



trishydroxy benzene

C_{3h}



C_{3v}

Properties of Matrices

Matrix: rectangular array of numbers or elements

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \quad a_{ij} \text{ } i^{\text{th}} \text{ row and } j^{\text{th}} \text{ column}$$

A vector is a one dimensional matrix

$$\begin{bmatrix} a_{11} \\ a_{21} \\ a_{31} \end{bmatrix}$$

This could be a set of Cartesian coordinates (x,y,z)

Matrix math basics

Addition and Subtraction

Matrices must be the same size

$c_{ij} = a_{ij} \pm b_{ij}$ add or subtract the corresponding elements in each matrix

Multiplication by a scalar (k)

$k[a_{ij}] = [ka_{ij}]$ every element is multiplied by the constant k

Matrix multiplication

$$\sum_k^n a_{ik} \times b_{kj} = c_{ij}$$

a_{ik} = element in the i^{th} row and k^{th} column

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \\ a_{31} & a_{32} \end{bmatrix} \times \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}$$

Where $c_{11} = (a_{11}b_{11} + a_{12}b_{21})$

$c_{12} = (a_{11}b_{12} + a_{12}b_{22})$

etc...

matrix multiplication is not commutative ($ab \neq ba$)

Matrix Division

Division is defined as multiplying by the inverse of a matrix. Only square matrices may have an inverse. The inverse of a matrix is defined as

$a \cdot a^{-1} = \delta_{ij}$ $\delta_{ij} \rightarrow$ Kronecker delta

$\delta_{ij} = 1$ if $i=j$ otherwise $\delta_{ij} = 0$

$$\delta_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Special Matrices

Block diagonal matrix multiplication

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 3 & 2 \\ 0 & 0 & 0 & 1 & 2 & 2 \\ 0 & 0 & 0 & 4 & 0 & 1 \end{bmatrix} \begin{bmatrix} 4 & 1 & 0 & 0 & 0 & 0 \\ 2 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 2 \\ 0 & 0 & 0 & 3 & 0 & 2 \\ 0 & 0 & 0 & 2 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 4 & 1 & 0 & 0 & 0 & 0 \\ 8 & 7 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 13 & 3 & 10 \\ 0 & 0 & 0 & 10 & 3 & 8 \\ 0 & 0 & 0 & 2 & 5 & 9 \end{bmatrix}$$

Each block is multiplied independently

i.e.

$$\begin{bmatrix} 1 & 0 \\ 1 & 2 \end{bmatrix} \begin{bmatrix} 4 & 1 \\ 2 & 3 \end{bmatrix} = \begin{bmatrix} 4 & 1 \\ 8 & 7 \end{bmatrix}$$

$$[3][1] = [3]$$

$$\begin{bmatrix} 1 & 3 & 2 \\ 1 & 2 & 2 \\ 4 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 2 \\ 3 & 0 & 2 \\ 2 & 1 & 1 \end{bmatrix} = \begin{bmatrix} 13 & 3 & 10 \\ 10 & 3 & 8 \\ 2 & 5 & 9 \end{bmatrix}$$

Square Matrices

$$\chi_a = \sum_j a_{jj}$$

This is the sum of the diagonal elements of a matrix (trace).

χ_a is call the character of a matrix

properties of χ

if $c = ab$ and $d = ba$ then $\chi_c = \chi_d$

conjugate matrices have identical χ

$r = b^{-1}pb$ then $\chi_r = \chi_b$

Operations that are in the same class have the same character.

Matrix Representations of Symmetry Operations

We will now use matrices to represent symmetry operations. Consider how an $\{x,y,z\}$ vector is transformed in space

Identity

E

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Reflection σ_{xy}

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}$$

 σ_{xz}

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

Inversion

i

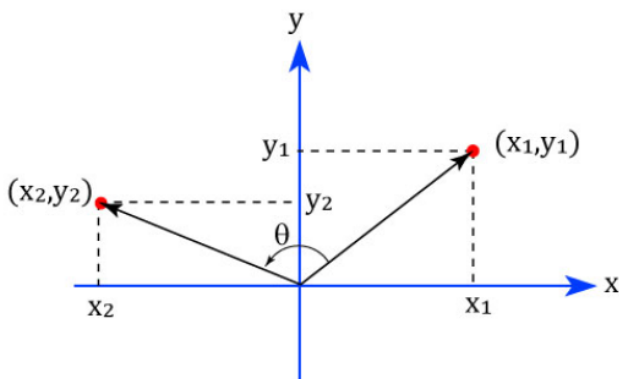
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

Rotation

C_n about the z axis

$$\begin{bmatrix} ? & ? & 0 \\ ? & ? & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z \end{bmatrix} \quad \text{The z coordinate remains unchanged.}$$

Consider a counter clockwise rotation by θ about the z axis



From trigonometry we know that

$$x_2 = x_1 \cos \theta - y_1 \sin \theta \quad \text{and} \quad y_2 = x_1 \sin \theta + y_1 \cos \theta$$

Represented in matrix form this gives:

$$\begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix}$$

For a clockwise rotation we find

$$\begin{bmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix} \quad \text{recall } \cos \phi = \cos(-\phi) \text{ and } \sin \phi = -\sin(-\phi)$$

The transformation matrix for a clockwise rotation by ϕ is:

$$\begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z \end{bmatrix}$$

Improper Rotations

S_n

Because an improper rotation may be expressed as $\sigma_{xy}C_n$ we can write the following since matrices also follow the associative law.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

$$\begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

The set of matrices that we have generated that transform a set of $\{x, y, z\}$ orthogonal coordinates are called orthogonal matrices. The inverse of these matrices is found by exchanging rows into columns (taking the transpose of the matrix).

Consider a C_3 rotation about the z-axis.

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = C_3$$

exchanging rows into columns gives

$$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = (C_3)^T = C_3^2$$

Multiplying these two matrices gives the identity matrix

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

We know from symmetry that $C_3 C_3^2 = C_3^2 C_3 = E$

Here we see that C_3 and C_3^2 are inverse and orthogonal to each other.

In general we can write a set of homomorphic matrices that form a representation of a given point group

For example, consider the water molecule which belongs to the C_{2v} group.

C_{2v} contains E , C_2 , σ_{xz} , σ_{yz}

The set of four matrices below transform and multiply exactly like the symmetry operations in C_{2v} . That is, they are homomorphic to the symmetry operations.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$E \qquad C_2 \qquad \sigma_{xz} \qquad \sigma_{yz}$

Show that $C_2 \sigma_{xz} = \sigma_{yz}$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The algebra of matrix multiplication has been substituted for the geometry of applying symmetry operations.

Character Tables

For C_{3v} we find the following character table with four regions.

C_{3v}	E	2 C_3	3 σ_v		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	Rz	
E	2	-1	0	(x,y)(Rx,Ry)	$(x^2-y^2, xy)(xz,yz)$
I		II		III	IV

Region I – Mulliken Symbols for Irreducible Representations

1) All 1×1 representations are “A” or “B”, 2×2 are “E” and 3×3 are “T”

- 2) 1×1 which are symmetric with respect to rotation by $2\pi/n$ about the principle C_n axis are "A" (i.e. the character is +1 under C_n). Those that are anti-symmetric are labeled "B" (the character is -1 under C_n).
- 3) Subscripts 1 or 2 are added to A and B to designate those that are symmetric (1) or anti-symmetric (2) to a $C_2 \perp$ to C_n or if no C_2 is present then to a σ_v .
- 4) ' and '' are attached to those that are symmetric (') or anti-symmetric ('') relative to a σ_h .
- 5) In groups with an inversion center (i), subscript g (German for gerade or even) is added for those that are symmetric with respect to i or a subscript u (German for ungerade or uneven) is added for those antisymmetric with respect to i.
- 6) Labels for E and T representations are more complicated but follow the same general rules.

Region II – Characters

This region list the characters of the irreducible representations for all symmetry operations in each group.

Region III – Translations and Rotations

The region assigns translations in x,y and z and rotations R_x , R_y , R_z to irreducible representations. E.g., in the group above (x,y) is listed in the same row as the E irreducible representation. This means that if one formed a matrix representation based on x and y coordinates, it would transform (that is have the same characters as) identically as E. Recall that previously we looked at a C_3 transformation matrix for a set of Cartesian coordinates

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = C_3$$

Notice that this matrix is block diagonalized. If we break this into blocks we are left with

$$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} x' \\ y' \end{bmatrix} = C_3 \text{ and } [1][z] = [z'] = C_3$$

Compare the characters of these matrices to the characters under C_3 in the table above. Notice that for (x,y) $\chi = -1$ and for (z) $\chi = 1$. If you compared the characters for all of the other transformation matrices you will see that (x,y) \rightarrow E and (z) \rightarrow A1 as shown in region III of the table. Similar analysis can be made with respect to rotations about x, y and z.

Region IV– Binary Products

This region list various binary products and to which irreducible representation that they belong. The d-orbitals have the same symmetry as the binary products. For example the d_{xy} orbital transforms the same as the xy binary product.

Representations of Groups

The following matrices form a representation of the C_{2v} point group

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

E C_2 σ_{xz} σ_{yz}

Group Multiplication Table for C_{2v}

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

How many other representations exist for the C_{2v} point group?

A: As many as we can think up

The set of numbers $\{1,1,1,1\}$ transform like C_{2v} etc...

However, there are only a few representations that are of fundamental importance.

Consider the matrices E, A, B, C, ... and we perform a similarity transform with Q

$$E' = Q^{-1}EQ$$

$$A' = Q^{-1}AQ$$

$$B' = Q^{-1}BQ$$

Etc...

For example $A' = Q^{-1}AQ$

$$A' = Q^{-1}AQ = \begin{array}{|c|c|c|c|} \hline A'_1 & & & \\ \hline & A'_2 & & \\ \hline & & A'_3 & \\ \hline & & & A'_4 \\ \hline \end{array}$$

The similarity transform of A by Q will block diagonalize all of the matrices

All of the resulting subsets form representations of the group as well

e.g. $E'_1, A'_1, B'_1 \dots etc \dots$

We say that E, A, B, C... are **reducible matrices** that form a set of **reducible representations**.

If Q does not exist which will block diagonalize all of the matrix representations then we have an **irreducible representation**.

Text Books:

1. Raman, K.V. (2002). Group theory. New Delhi: Tata Mc Graw Publishing Company.
2. Puri, Sharma & Pathania, (2006). Principles of Physical Chemistry. Jalandar: Millenium Edition, Vishal Publishing Co.
3. Veera Reddy, K. (2005). Symmetry and Spectroscopy of Molecules. New Delhi: New Age International Pvt. Ltd.

Possible Questions

PART- A Questions

(Each question carry one mark)

- Evidence in favour of the wave nature of radiation
 - Interference of radiation**
 - Photoelectric effect
 - Compton effect
 - Black body radiation
- Black body radiation has a characteristic
 - Continuous spectrum**
 - Discontinuous spectrum
 - Narrow range of light
 - Laser action
- As per plancks law the characteristic continuous spectrum of radiation depends upon
 - Body's temperature**
 - Nature of the body
 - Colour of the body
 - Density of the body
- Stefan Boltzmann law is based on
 - Diffraction of radiation
 - Photoelectric effect
 - Compton effect
 - Black body radiation**
- In one dimensional box problem the potential energy of the particle inside the box is
 - zero**
 - unity
 - infinity
 - fractional
- The solution of the problem of the rigid rotator gives us directly the solution of the
 - angular momentum operator**
 - Lapalacian operator
 - Hermitian operator
 - Position operator
- A diatomic vibrating molecule can be represented by a simple model called
 - Simple harmonic oscillator**
 - Rigid rotor
 - Particle in one dimensional box
 - Particle in three dimensional box
- The quantum number 'n' is called
 - Principal quantum number**
 - Azimuthal quantum number
 - Magnetic quantum number
 - Angular momentum quantum number
- The lowest energy orbital for the ammonia molecule is designated
 - 1s
 - $1\sigma_g$
 - $1a_1$**
 - C_{3v}
- The benzene molecule C_6H_6 has how many vibrational modes
 - 6
 - 12
 - 24
 - 30**
- The method applicable for a system which wave functions may be guessed
 - Perturbation method
 - Variation method**
 - Normalization of the wave function
 - d. Making the wave functions orthogonal
- Write the energy level for the free particle in motion
 - $E_n=2n-1/2$
 - $E_n=n^2$
 - E_n is continuous**
 - $E_n \propto n^2$
- The shape of $BeCl_2$ molecules is
 - Linear**
 - Triangular planar
 - Tetrahedral
 - octahedral
- Example for tetrahedral molecule
 - $BeCl_2$
 - boron trifluoride
 - methane**
 - phosphorous pentachloride

15. If the symmetry element is the 'plane of symmetry' then the corresponding symmetry operation is
a. Doing nothing b. **reflection** c. Inversion of all coordinates
d. Rotation through an angle of $360/n$ about an axis where 'n' is the order of the axis
16. For the symmetry operation "rotation" the corresponding symmetry element is
a. Identity element b. Plane of symmetry
c. Centre of symmetry d. **Proper axis of symmetry**
17. The basic theorem is concerned with the elements of the matrices constituting the irreducible representation of a group is called
a. Faradays theorem b. **The great orthogonality theorem**
c. Normalized theorem d. Van der Waals theorem
18. Character tables are constructed using
a. Symmetry elements b. **Orthogonality theorem**
c. Symmetry operations d. Irreducible operations
19. The corresponding matrix for the operation E is
a. Zero matrix b. Square matrix c. Diagonal matrix d. **Unit matrix**
20. Reducible representation is also called as
a. **Total character** b. Symmetry elements
c. Symmetry operations d. Total elements of symmetry

PART- B Questions

(Each questions carries six marks)

21. (a). Explain the failure of classical mechanics and the success of quantum theory in explaining the results of black body radiation experiment.
(OR)
(b). Write notes on photoelectric effect.
22. (a). Solve the Schrodinger wave equation for one dimensional harmonic oscillator for its energy.
(OR)
(b) Solve the Schrodinger wave equation for one dimensional harmonic oscillator for its energy.
23. (a). Explain perturbation method and arrive at the expression for the first order correction to energy and wave function.
(OR)
(b). Explain the application of variation method to anharmonic oscillator and Helium atom.
24. (a). (i) What is a group?
(ii) What are the defining properties of a group?
(iii) Define class.
(OR)
(b). (i) What are the conditions for the elements to form a group.

(ii) Define abelian and cyclic groups. Prove the statement. Every cyclic group is abelian but the converse is not true.

25. (a). Explain the symmetry selection rules for infra-red and Raman spectra.

(OR)

(b). (i) State direct product rule? Illustrate its applications.

(ii) Write the simple procedure to determine hybridization pattern in sigma bond.

PART- C Question

(Each questions carries ten marks)

26. Solve the Schrodinger wave equation for a particle in one dimensional box for its energy and show that the energy states are orthogonal.



KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2017 & onwards)
Group Theory

Multiple Choice Questions for Unit IV

S. No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	The shape of boron trifluoride is	Linear	Triangular planar	Tetrahedral	octahedral	Linear
2	The structure of methane is	Linear	Triangular planar	Tetrahedral	octahedral	Triangular planar
3	The structure of phosphorous pentachloride is	Linear	Trigonal bipyramidal	Tetrahedral	octahedral	tetrahedral
4	Example for a linear molecule	BeCl ₂	boron trifluoride	methane	phosphorous pentachloride	BeCl ₂
5	Example for triangular planar molecule	BeCl ₂	boron trifluoride	methane	phosphorous pentachloride	boron trifluoride
6	Example for tetrahedral molecule	BeCl ₂	boron trifluoride	methane	phosphorous pentachloride	methane
7						

8	Example for Trigonal bipyramidal	BeCl_2	boron trifluoride	methane	phosphorous pentachloride	phosphorous pentachloride
9	One of the following is an geometric operation when performed on the molecule, give rise to an indistinguishable configuration of the same molecule	Diffraction	interference	polarisation	reflection	reflection
10	One of the following is an geometric operation when performed on the molecule, give rise to an indistinguishable configuration of the same molecule	Diffraction	interference	polarisation	rotation	Rotation
11	One of the following is an geometric operation when performed on the molecule, give rise to an indistinguishable configuration of the same molecule	Diffraction	interference	polarisation	inversion	inversion
12	If the symmetry element is the 'identity element' then the corresponding symmetry operation is	Doing nothing	reflection	Inversion of all coordinates	Rotation through an angle of $360/n$ about an axis where 'n' is the order of the axis	Doing nothing
13	If the symmetry element is the 'plane of symmetry' then the corresponding symmetry operation is	Doing nothing	reflection	Inversion of all coordinates	Rotation through an angle of $360/n$ about an axis where 'n' is the order of the axis	reflection

14	If the symmetry element is the ‘proper axis of symmetry ’ then the corresponding symmetry operation is	Doing nothing	reflection	Inversion of all coordinates	Rotation through an angle of $360/n$ about an axis where ‘n’ is the order of the axis	Rotation through an angle of $360/n$ about an axis where ‘n’ is the order of the axis
15	If the symmetry element is the ‘centre of symmetry ’ then the corresponding symmetry operation is	Doing nothing	reflection	Inversion of all coordinates	Rotation through an angle of $360/n$ about an axis where ‘n’ is the order of the axis	Inversion of all coordinates
16	If the symmetry element is the ‘improper axis of symmetry ’ then the corresponding symmetry operation is	Doing nothing	reflection	Inversion of all coordinates	Rotation through an angle of $360/n$ about an axis followed by reflection	Rotation through an angle of $360/n$ about an axis followed by reflection
17	For the symmetry operation “doing nothing” the corresponding symmetry element is	Identity element	Plane of symmetry	Centre of symmetry	Proper axis of symmetry	Identity element
18	For the symmetry operation “reflection” the corresponding symmetry element is	Identity element	Plane of symmetry	Centre of symmetry	Proper axis of symmetry	Plane of symmetry
19	For the symmetry operation “Rotation through an angle of $360/n$ about an axis where ‘n’ is the order of the axis” the corresponding symmetry element is	Identity element	Plane of symmetry	Centre of symmetry	Proper axis of symmetry	Proper axis of symmetry

20	For the symmetry operation 'Rotation through an angle of $360/n$ about an axis followed by reflection' the corresponding symmetry element is	Identity element	Plane of symmetry	Centre of symmetry	improper axis of symmetry	improper axis of symmetry
21	Molecules which have an infinite number of planes of symmetry	Linear molecules	Tetrahedral molecules	Octahedral molecules	Triangular molecules	Linear molecules
22	Molecules which have an infinite number of planes of symmetry	acetylene	methane	Boron trifluoride	Phosphorous pentachloride	acetylene
23	Molecules which have an infinite number of planes of symmetry	BeCl_2	methane	Boron trifluoride	Phosphorous pentachloride	BeCl_2
24	The number of plane of symmetry for Acetylene molecule is	one	two	three	infinity	infinity
25	The number of plane of symmetry for a linear molecule is	one	two	three	infinity	infinity
26	The number of plane of symmetry for a BeCl_2 molecule is	one	two	three	infinity	infinity
27	Which molecules have the molecular plane as one of the plane of symmetry	Planar	triangular	tetrahedral	octahedral	Planar
28	The molecule which possess two planes of symmetry is	BeCl_2	water	Boron trifluoride	Phosphorous pentachloride	water
29	The molecule which possesses C_∞ axis of symmetry is					Matrices
30	An array of numbers arranged in rows and columns are called	Matrices	determinants	Space lattices	Miller indices	Point groups

31	A collection of the symmetry elements present in a molecule that obeys the mathematical rules for the formation of a group are called	Point groups	Space groups	Space lattices	Miller indices	An equal number of rows and columns
32	A square matrix will have	An equal number of rows and columns	An unequal number of rows and columns	Only rows	Only columns	Square matrix
33	A matrix with an equal number of rows and columns	Square matrix	Diagonal matrix	Null matrix	Unit matrix	Diagonal matrix
34	In a square matrix if all the elements other than those along the diagonal are zero, it is called	Diagonal matrix	Null matrix	Unit matrix	Transpose of a matrix	In a square matrix if all the elements other than those along the diagonal are zero
35	A diagonal matrix will have	In a square matrix if all the elements other than those along the diagonal are zero	In a square matrix if all the elements other than those along the diagonal are unity	In a square matrix if all the elements along the diagonal are unity	In a square matrix if all the elements along the diagonal are zero	If every element of a diagonal matrix is one (1)
36	Unit matrix	If every element of a diagonal matrix is one (1)	If every element of a square matrix is one (1)	If every element of a null matrix is one (1)	If every element of a null matrix is zero	Unit matrix

37	If every element of a diagonal matrix is one (1)	Unit matrix	Square matrix	Diagonal matrix	Transpose of a matrix	C_1
39	Example for a low symmetry point group	C_s	D_2	C_{2h}	S_4	C_i
41	The molecule with $D_{\infty h}$ point group	acetylene	water	ammonia	Boron trichloride	water
42	The molecule with C_{2v} point group	acetylene	water	ammonia	Boron trichloride	ammonia
43	The molecule with C_{3v} point group	acetylene	water	ammonia	Boron trichloride	Boron trichloride
44	The molecule with D_{3h} point group	acetylene	water	ammonia	Boron trichloride	$D_{\infty h}$
45	The point group of acetylene is	$D_{\infty h}$	C_{2v}	C_{3v}	D_{3h}	C_{2v}
46	The point group of water is	$D_{\infty h}$	C_{2v}	C_{3v}	D_{3h}	C_{3v}
47	The point group of ammonia is	$D_{\infty h}$	C_{2v}	C_{3v}	D_{3h}	D_{3h}
48	The point group of boron trichloride is	$D_{\infty h}$	C_{2v}	C_{3v}	D_{3h}	32
49	The number of possible point groups for a crystal is	32	45	62	7	Six
50	The maximum number of axis of symmetry a crystal can have is	two	Three	Four	six	Block factored matrix
51	A matrix in which all the non-zero elements will be in square blocks along the diagonal	Block factored matrix	Character os a matrix	Square matrix	Diagonal matrix	Matrix which will also be blocked out in exactly the same way

52	If two similiarly blocked out matrices are multiplied, the product will be a	Matrix which will also be blocked out in exactly the same way	Diagonal matrix	Square matrix	Unit matrix	A coordinatio n point (x,y,z) in the Cartesian coordinates
53	A one column matrix represents	A coordinatio n point (x,y,z) in the Cartesian coordinates	A scalar matrix	Unit matrix	Diagonal matrix	matrix
54	Multiplication of two matrices gives a	matrix	determinant	Scalar product	Vector product	commutative
55	Multiplication of a matrix with unit matrix is	commutative	Non-commutative	associative	Non-associative	Leaves the matrix unchanged
56	Multiplication of a matrix with unit matrix is	Leaves the matrix unchanged	Matrix will be squared	Matrix will be divided by the number of rows	Matrix will be divided by the number of columns	Carbonyl sulfide
57	The molecule with $C_{\alpha v}$ point group	Carbonyl sulfide	water	ammonia	Boron trichloride	Dichloro methane
58	The molecule with C_{2v} point group	acetylene	Dichloro methane	ammonia	Boron trichloride	Nitrogen trifluoride
59	The molecule with C_{3v} point group	acetylene	water	Nitrogen trifluoride	Boron trichloride	ethylene

60	The molecule with D_{2h} point group	acetylene	water	ammonia	ethylene	Vinca alkaloids
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UNIT – V

IR/Raman spectroscopy

Definition of reducible and irreducible representations - irreducible representations as orthogonal vectors - direct product rule, the great orthogonality theorem and its consequences - determinations of the characters for irreducible representation of C_{2v} and C_{3v} point groups using the orthogonality theorem.

Group theory and Vibrational spectroscopy - vibrational modes as basis for group representation - symmetry selection rules for IR and Raman spectra, Mutual exclusion principle - classification of vibrational modes. Group theory and dipole moment.

The Great Orthogonality Theorem

The theorem states

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

Terms

h = order of the group (# of symmetry operators)

T_i = i th representation

l_i = dimension of T_i (e.g. 3×3 , $l_i = 3$)

R = generic symbol for an operator

$[T_i R(mn)]$ = the element in the m th row and n th column of an operator R in representation T_i

$[T_j R(m'n')]^*$ = complex conjugate of the element in the m' th row and n' th column of an operator R in representation T_j .

What does this all mean?

For any two irreducible representations T_i, T_j

Any corresponding matrix elements (one from each matrix) behave as components of a vector in h -dimensional space, such that all vectors are orthonormal. That is, orthogonal and of unit length.

Examine the theorem under various conditions...

If vectors are from different representations then they are orthogonal

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)_{m'n'}]^* = 0 \text{ if } i \neq j$$

If vectors are from the same representation but are different sets of elements then they are orthogonal

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)_{m'n'}]^* = 0 \text{ if } m \neq m' \text{ or } n \neq n'$$

The square of the length of any vector is h/l_i

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)_{mn}]^* = \frac{h}{l_i}$$

Irreducible Representations

There are five important rules concerning irreducible representations

1) The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group

$$\sum_i l_i^2 = h$$

2) The sum of the squares of the characters in an irreducible representation is equal to the order of the group

$$\sum_i [\chi_i(R)]^2 = h$$

3) Vectors whose components are the characters of two irreducible representations are orthogonal

$$\sum_i [\chi_i(R)] [\chi_j(R)] = 0 \text{ when } i \neq j$$

4) In a given representation (reducible or irreducible) the characters of all matrices belonging to the same class are identical

5) The number of irreducible representations of a group is equal to the number of classes in the group.

Let's look at a simple group, C_{2v} (E, C₂, σ_v, σ_v)

There are four elements each in a separate class. By rule 5, there must be 4 irreducible representations. By rule 1, the sum of the squares of the dimensions must be equal to h (4).

$$l_1^2 + l_2^2 + l_3^2 + l_4^2 = 4$$

The only solution is $l_1 = l_2 = l_3 = l_4 = 1$

Therefore the C_{2v} point group must have four one dimensional irreducible representations.

All other representations must satisfy $\sum_i [\chi_i(R)]^2 = 4$

This can only work for $\chi_i = \pm 1$. And for each of the remaining Γ to be orthogonal to Γ_1 there must be two +1 and two -1.

Therefore, the remaining Γ must be (E is always +1)

C_{2v}	E	C_2	σ_v	σ_v'
Γ_1	1	1	1	1
Γ_2	1	-1	-1	1
Γ_3	1	-1	1	-1
Γ_4	1	1	-1	-1

Take any two and verify that they are orthogonal

$$\Gamma_1 \Gamma_2 = (1 \times 1) + (1 \times -1) + (1 \times -1) + (1 \times 1) = 0$$

These are the four irreducible representation of the point group C_{2v}

Consider the C_{3v} group (E, $2C_3$, $3\sigma_v$)

There are three classes so there must be three irreducible representations

$$l_1^2 + l_2^2 + l_3^2 = 6$$

The only values which work are $l_1 = 1, l_2 = 1, l_3 = 2$

That is, two one dimensional representations and one two dimensional representation.

So for Γ_1 we can choose

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1

For Γ_2 we need to choose ± 1 to keep orthogonality

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1

$$\Gamma_1 \Gamma_2 = (1 \times 1) + 2(1 \times -1) + 3(1 \times -1) = 0$$

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2		

To find Γ_3 we must solve the following

$$\sum_i [\chi_1(R)][\chi_3(R)] = (1)(2) + 2(1)[\chi_3(C_3)] + 3(1)[\chi_3(\sigma_v)] = 0$$

$$\sum_i [\chi_2(R)][\chi_3(R)] = (1)(2) + 2(1)[\chi_3(C_3)] + 3(-1)[\chi_3(\sigma_v)] = 0$$

Solving this set of two equation and two unknowns gives

$$[\chi_3(C_3)] = -1 \text{ and } [\chi_3(\sigma_v)] = 0$$

Therefore the complete set of irreducible representations is

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

We have derived the character tables for C_{2v} and C_{3v} (check the book appendix)

C_{2v}	E	C_2	σ_v	σ_v'	C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1	1	A_1	1	1	1
A_2	1	-1	-1	1	A_2	1	1	-1

$$\begin{array}{c|cccc}
 B_1 & 1 & -1 & 1 & -1 \\
 B_2 & 1 & 1 & -1 & -1
 \end{array}
 \qquad
 \begin{array}{c|ccc}
 E & 2 & -1 & 0
 \end{array}$$

We now know that there is a similarity transform that may block diagonalize a reducible representation. During a similarity transform the character of a representation is left unchanged.

$$\chi(R) = \sum_j a_j \chi_j(R)$$

Where $\chi(R)$ is the character of the matrix for operation R and a_j is the number of times that the j^{th} irreducible representation appears along the diagonal.

The good news is that we do not need to find the matrix Q to perform the similarity transform and block diagonalize the matrix representations. Because the characters are left intact, we can work with the characters alone.

We will multiply the above by $\chi_i(R)$ and sum over all operations.

$$\sum_R \chi(R) \chi_i(R) = \sum_R \sum_j a_j \chi_j(R) \chi_i(R) = \sum_j \sum_R a_j \chi_j(R) \chi_i(R)$$

and

$$\sum_R \chi_i(R) \chi_j(R) = h \delta_{ij}$$

For each sum over j we have

$$\sum_R a_j \chi_j(R) \chi_i(R) = a_j \sum_R \chi_j(R) \chi_i(R) = a_j h \delta_{ij}$$

The characters for χ_i and χ_j form orthogonal vectors we can only have non-zero values when $i \neq j$

The Reduction Formula

The above leads to the important result called “The Reduction Formula”

$$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

Where a_i is the number of times the i^{th} irreducible representation appears in the reducible representation.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ_a	5	2	-1
Γ_b	7	1	-3

Apply the reduction formula to Γ_a and Γ_b

For Γ_a

$$a_1 = \frac{1}{6} [(1)(1)(5) + (2)(1)(2) + (3)(1)(-1)] = 1$$

$$a_2 = \frac{1}{6} [(1)(1)(5) + (2)(1)(2) + (3)(-1)(-1)] = 2$$

$$a_3 = \frac{1}{6} [(1)(2)(5) + (2)(-1)(2) + (3)(0)(-1)] = 1$$

For Γ_b

$$a_1 = \frac{1}{6}[(1)(1)(7) + (2)(1)(1) + (3)(1)(-3)] = 0$$

$$a_2 = \frac{1}{6}[(1)(1)(7) + (2)(1)(1) + (3)(-1)(-3)] = 3$$

$$a_3 = \frac{1}{6}[(1)(2)(7) + (2)(-1)(1) + (3)(0)(-3)] = 2$$

Sum the columns...

For Γ_a

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ_a	5	2	-1

For Γ_b

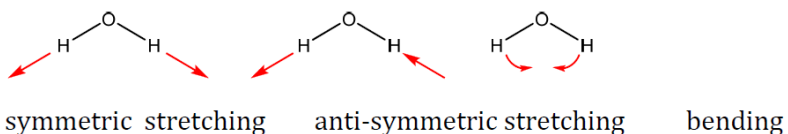
C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_2	1	1	-1
Γ_2	1	1	-1
Γ_2	1	1	-1
Γ_3	2	-1	0
Γ_3	2	-1	0
Γ_b	7	1	-3

Vibrations

We can use the tools of group theory to deduce the qualitative appearance of the normal modes of vibration.

We'll start with a simple molecule like H₂O.

For water we expect $3N-6 = 3$ normal modes of vibration. Water is simple enough that we can guess the modes.



Assign these three vibrations to irreducible representations in the C_{2v} point group.

C _{2v}	E	C ₂	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	
A ₁	1	1	1	1	z
A ₂	1	1	-1	-1	R _z
B ₁	1	-1	1	-1	x, R _y
B ₂	1	-1	-1	1	y, R _x

Consider the displacement vectors (red arrows) for each mode and write what happens under each symmetry operation.

Symmetric stretching (Γ^{v1})

$$E \rightarrow 1, C_2 \rightarrow 1, \sigma_{(xz)} \rightarrow 1, \sigma'_{(yz)} \rightarrow 1$$

Anti - Symmetric stretching (Γ^{v2})

$$E \rightarrow 1, C_2 \rightarrow -1, \sigma_{(xz)} \rightarrow 1, \sigma'_{(yz)} \rightarrow -1$$

Bending (Γ^{v3})

$$E \rightarrow 1, C_2 \rightarrow -1, \sigma_{(xz)} \rightarrow 1, \sigma'_{(yz)} \rightarrow -1$$

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma'_{(yz)}$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x
Γ^{v1}	1	1	1	1	
Γ^{v2}	1	-1	1	-1	
Γ^{v3}	1	1	1	1	

In a more complicated case we would apply the reduction formula to find the Γ_{irr} which comprise Γ_v . However, in this case we see by inspection that

$$\Gamma^{v1} \rightarrow A_1$$

$$\Gamma^{v2} \rightarrow B_1$$

$$\Gamma^{v3} \rightarrow A_1$$

Selection Rules for Vibrations

Born-Oppenheimer approximation: electrons move fast relative to nuclear motion.

$$\psi = \psi_{el}\psi_N$$

$$\iint \psi_{el}^* \psi_N^* \hat{d} \psi_{el} \psi_N' d\tau_{el} d\tau_N$$

Where:

ψ_{el} is the electronic wavefunction and ψ_N is the nuclear wavefunction

\hat{d} is the dipole moment operator

$$\hat{d} = \sum_i (-e)r_i + \sum_{\alpha} Z_{\alpha}er_{\alpha}$$

Where:

r_i is the radius vector from the origin to a charge q_i (an electron in this case)

$-e$ is the proton charge $Z\alpha$ is the nuclear charge, r_α is the radius vector for a nucleus

Integrals of this type define the overlap of wavefunctions. When the above integral is not equal to 0, a vibrational transition is said to be allowed. That is, there exists some degree of overlap of the two wavefunctions allowing the transition from one to the other.

In 1800 Sir William Herschel put a thermometer in a dispersed beam of light. When he put the thermometer into the region beyond the red light he noted the temperature increased even more than when placed in the visible light. He had discovered infrared (IR) light.

Similar to electronic transitions with visible and UV light, IR can stimulate transitions from $v_1 \rightarrow v_2$. A simplified integral describing this transition is

$$\int \psi_0^{vib*} \hat{d} \psi_m^\rho d\tau$$

which is allowed when the integral does not equal zero.

In this integral

ψ_0^{vib*} = vibrational ground state wavefunction and ψ_m^ρ is the ρ th fundamental vibrational level wavefunction.

What this all means is that a vibrational transition in the infrared region is only allowed if the vibration causes a change in the dipole moment of the molecule.

Dipole moments translate just like the Cartesian coordinate vectors x, y and z. Therefore only vibrations that have the same symmetry as x, y or z are allowed transitions in the infrared.

Selection Rules for Raman Spectroscopy

In Raman spectroscopy, incident radiation with an electric field vector E may induce a dipole in a molecule. The extent of which depends on the polarizability of the molecule (α_{ij} polarizability operator).

$$\int \psi_0^{vib*} \alpha_{ij} \psi_m^\rho d\tau$$

Transitions in Raman spectroscopy are only allowed if the vibration causes a change in polarizability.

Polarizability transforms like the binary product terms (xy, z^2 etc...) and therefore vibrations that have the same symmetry as the binary products are allowed transitions in Raman spectroscopy. For water, all three vibrations are IR and Raman active.

SUGGESTED READINGS:

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3. House Ames, E. (2005). Fundamental of Quantum Chemistry. New Delhi: II Elsevier Academic Press.
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1. Raman, K.V. (2002). Group theory. New Delhi: Tata Mc Graw Publishing Company.
2. Puri, Sharma & Pathania, (2006). Principles of Physical Chemistry. Jalandar: Millenium Edition, Vishal Publishing Co.
3. Veera Reddy, K. (2005). Symmetry and Spectroscopy of Molecules. New Delhi: New Age International Pvt. Ltd.
4. Peter Atkins and Julio de Paula. (2009). Atkins' Physical chemistry. Noida. Oxford University press. Gopsons papers Ltd.

Possible Questions**PART- A Questions****(Each question carries one mark)**

1. The power emitted per unit area of the surface of a black body is directly proportional to the fourth power of its absolute temperature, the law is
 - a. **Stefan Boltzmann law**
 - b. Weins displacement law
 - c. Planck's law
 - d. Jean's law
2. Evidence in favour of the particle nature of radiation
 - a. Diffraction of radiation
 - b. **Compton effect**
 - c. polarization
 - d. interference
3. Black body radiation has a characteristic continuous spectrum of radiation which depends upon
 - a. **Body's temperature**
 - b. Nature of the body
 - c. Colour of the body
 - d. Density of the body
4. The spectrum of black-body radiation at any temperature is related to the spectrum at any other temperature
 - a. Stefan Boltzmann law
 - b. **Weins displacement law**
 - c. Planck's law
 - d. Jean's law
5. In one dimensional box problem the potential energy of the particle outside the box is
 - a. zero
 - b. unity
 - c. **infinity**
 - d. fractional
6. The energy levels of the particle in the box are
 - a. quantized
 - b. randomized
 - c. dispersed
 - d. Not-quantized
7. The theory of rigid rotor in space is useful in dealing with
 - a. **Rotational spectra of diatomic molecules**
 - b. Vibrational spectra of diatomic molecules
 - c. IR spectra of diatomic molecules
 - d. Raman spectra of diatomic molecules
8. In the Hook's law $f = -kx$, k is called
 - a. **Force constant**
 - b. Gas constant
 - c. Boltzmann constant
 - d. Faraday's constant
9. An one electron system whose potential field is not spherically symmetrical

- a. Hydrogen atom b. **Hydrogen atom in electric field**
 - c. Hydrogen molecule d. Helium molecule
10. The method to obtain approximate solutions to the wave equation
a. **Perturbation method** b. Normalization of the wave function
c. Making the wave functions orthogonal d. making the wave functions orthonormal
11. Zeeman effect is
a. **the change in energy levels of an atom when it is placed in uniform external field** b.
The change in energy levels of an atom when placed in non-uniform external field c. The
change in energy levels of an atom when placed in external electric field d. The change in
energy levels of an atom when placed in non-uniform electric field
12. The energy level belongs to $E_n = -2n^{-1/2}$
a. **Harmonic oscillator** b. Hydrogen atom
c. particle in a box d. free particle in motion
13. For the symmetry operation "reflection" the corresponding symmetry element is
a. Identity element b. **Plane of symmetry**
c. Centre of symmetry d. Proper axis of symmetry
14. An array of numbers arranged in rows and columns are called
a. **Matrices** b. determinants c. Space lattices d. Miller indices
15. A diagonal matrix will have
a. **In a square matrix if all the elements other than those along the diagonal are zero**
b. In a square matrix if all the elements other than those along the diagonal are unity
c. In a square matrix if all the elements along the diagonal are unity
d. In a square matrix if all the elements along the diagonal are zero
16. The molecule with C_{3v} point group
a. acetylene b. water c. **ammonia** d. Boron trichloride
17. For a pyramidal molecule with point group C_{3v} the number of theoretically predicted IR
fundamental bands
a. **Three** b. Four c. Five d. Six
18. For chloro trifluoride molecule the number of observed Raman bands and IR bands are four
each, the predicted geometry is
a. Pyramidal b. planar c. **T-shaped** d. bent
19. In case of molecules with a centre of symmetry the vibrational modes are anti-symmetric to
centre of inversion are
a. IR inactive b. **IR active** c. Raman inactive d. Raman hyper active
20. For Raman activity the vibrations should involve a change in
a. **polarizability** b. magnetization c. Magnetic susceptibility d. Surface tension

PART- B Questions

(Each questions carries six marks)

21. a. What are the postulates of Quantum mechanics?
(OR)
b. What are operators in quantum mechanics? Explain multiplication of operators.

22. (a). Set up Schrodinger wave equation for the rigid rotor of diatomic molecule.

(OR)

(b). Set up Schrodinger wave equation for one dimensional box and solve the equation for its energy.

23. (a). What are the applications of perturbation method to anharmonic oscillator and Helium atom.

(OR)

(b). Derive Schrodinger equation for H-atom.

24. (a) (i) Define class and sub –group.

(ii) Write notes on similarity transformation.

(iii) Show that the element $[1, -1, i, -i]$ form a group.

(OR)

(b). (i) Prove the following:

$$S_4^4 = E, \quad S_3^3 = \sigma_h, \quad S_5^4 = C_5^4, \quad S_4^2 = C_2$$

(ii) Distinguish between vertical plane and horizontal plane.

(iii) Prove that $C_2(x) C_2(y) = C_2(z)$.

25. (a) (i) What are the relationship between reducible and irreducible representation of the group.

(ii) What are the properties of irreducible representation?

(OR)

(b) (i) State and explain the great orthogonality theorem.

(ii) How will you construct the character table for a C_{2v} and C_{3v} point group using the great orthogonality theorem?

PART- C Question

(Each Question carries ten marks)

26. What is meant by zeropoint energy? Show that the zero point energy for a particle in one dimensional box is in accordance with Heisenberg's principle



KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University Under Section 3 of UGC Act 1956)
COIMBATORE-21

DEPARTMENT OF CHEMISTRY
(For the candidates admitted from 2017 & onwards)
Group Theory

Multiple Choice Questions for Unit V

S. No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	For a planar molecule with point group D_{3h} the number of theoretically predicted IR fundamental bands	Three	Four	Five	Six	Three
2	For a planar molecule with point group D_{3h} the number of theoretically predicted Raman fundamental bands	Three	Four	Five	Six	Three
3	For a pyramidal molecule with point group C_{3v} the number of theoretically predicted Raman fundamental bands	Three	Four	Five	Six	four
4	For a pyramidal molecule with point group C_{3v} the number of theoretically predicted IR fundamental bands	Three	Four	Five	Six	four
5	For a T-shaped molecule with point group C_{3v} the number of theoretically predicted IR fundamental bands	Three	Four	Five	Six	six

6	For a T-shaped molecule with point group C_{3v} the number of theoretically predicted Raman fundamental bands	Three	Four	Five	Six	six
7	For Phosphorous trichloride molecule the number of observed IR bands	Three	Four	Five	Six	four
8	For Boron trifluoride molecule the number of observed IR bands	Three	Four	Five	Six	three
9	For chloro trifluoride molecule the number of observed IR bands	Three	Four	Five	Six	Six
10	For Phosphorous trichloride molecule the number of observed Raman bands	Three	Four	Five	Six	four
11	For Boron trifluoride molecule the number of observed Raman bands	Three	Four	Five	Six	three
12	For chloro trifluoride molecule the number of observed Raman bands	Three	Four	Five	Six	Six
13	For Phosphorous trichloride molecule the number of observed Raman bands and IR bands are three each, the predicted geometry is	Pyramidal	planar	T-shaped	bent	Pyramidal
14	For Boron trifluoride molecule the number of observed Raman bands and IR bands are four each, the predicted geometry is	Pyramidal	planar	T-shaped	bent	Planar
15	For chloro trifluoride molecule the number of observed Raman bands and IR bands are four each, the predicted geometry is	Pyramidal	planar	T-shaped	bent	T-shaped
16	In the IR and Raman spectra, apart from the fundamental absorption bands, it contains	overtones	Metastable bands	Solvent bands	Base bands	overtones

17	In the IR and Raman spectra, apart from the fundamental absorption bands, it contains	Combination bands	Metastable bands	Solvent bands	Base bands	Combination bands
18	In case of molecules with a centre of symmetry the vibrational modes symmetric to centre of inversion are	IR inactive	IR active	Raman inactive	Raman hyperactive	IR inactive
19	In case of centrosymmetric molecules, the IR active vibrational modes are Raman inactive and Raman active vibrational modes are IR inactive, the principle is called	Paulis exclusion principle	Mutual exclusion principle	Hund's rule	Overtone rule	Mutual exclusion principle
20	In case of molecules with a centre of symmetry the vibrational modes are anti-symmetric to centre of inversion are	IR inactive	IR active	Raman inactive	Raman hyperactive	IR active
21	Vibrations of 'g' modes are	IR inactive	IR active	Raman active	Raman hyperactive	Raman active
22	Vibrations of 'u' modes are	IR inactive	IR active	Raman inactive	Raman hyperactive	Raman inactive
23	IR active vibrations involve a change in	Dipole moment	magnetization	Magnetic susceptibility	Surface tension	Dipole moment
24	For Raman activity the vibrations should involve a change in	polarizability	magnetization	Magnetic susceptibility	Surface tension	polarizability
25	For Raman activity the vibrations should involve a change in	Induced dipole moment	magnetization	Magnetic susceptibility	Surface tension	polarizability
26	The basic theorem is concerned with the elements of the matrices constituting the irreducible representation of a group is called	Faradays theorem	The great orthogonality theorem	Normalized theorem	Van der Waals theorem	The great orthogonality theorem
27	All the properties of group representations and their characters can be derived from this theorem	Faradays theorem	The great orthogonality theorem	Normalized theorem	Van der Waals theorem	The great orthogonality theorem

28	The Kronecker delta can have values	1 or 0	1 or 2	0 or 2	1 Or 3	1 or 0
29	According to the great orthogonality theorem the sum over various operations of the products of the elements of irreducible representations will be equal to	zero	An odd number	An even number	Positive number	zero
30	As per the Great Orthogonality theorem, the number of irreducible representations in a group is equal to the number of	Symmetry elements	classes of elements in the group	Symmetry operations	Matrix elements	classes of elements in the group
31	As per the Great Orthogonality theorem, in a given representation the characters of all the elements of the same class will be	identical	different	dissimilar	interactive	identical
32	As per the Great Orthogonality theorem, the sum of the squares of the dimensions of the irreducible representations of a group will be equal to the	Order of the group	classes of elements in the group	Symmetry operations	Matrix elements	Order of the group
33	As per the Great Orthogonality theorem, the sum of the squares of the characters in a given irreducible representations of a group will be equal to the	Order of the group	classes of elements in the group	Symmetry operations	Matrix elements	Order of the group
34	As per the Great Orthogonality theorem, the characters of any two irreducible representations of a group are	orthogonal	normalised	orthonormal	identical	orthogonal
35	In the construction of the character table One dimensional irreducible representation will be denoted by	A or B	E	T	U	A or B
36	In the construction of the character table two dimensional irreducible representation will be denoted by	A or B	E	T	U	E

37	In the construction of the character table Three dimensional irreducible representation will be denoted by	A or B	E	T	U	T
38	Character tables are constructed using	Symmetry elements	Orthogonality theorem	Symmetry operations	Irreducible operations	Orthogonality theorem
39	One of the following is not true with respect to the information's to the character table	The number of IR's possible for a point group	The symmetry and corresponding fundamental bases for very few IR	The name of the point group with the possible symmetry elements	The character corresponding to various classes of symmetry elements for all the IRs	The symmetry and corresponding fundamental bases for very few IR
40	Null matrix is also called as	Zero matrix	Square matrix	Diagonal matrix	Unit matrix	Zero matrix
41	The corresponding matrix for the operation E is	Zero matrix	Square matrix	Diagonal matrix	Unit matrix	Unit matrix
42	In C_{2v} point group the number of irreducible representation are possible	Four	five	six	three	Four
43	In C_{3v} point group the number of irreducible representation are possible	Four	five	six	three	Three
44	The number of elements present in C_{3v} point group	Four	five	six	three	six
45	The order of the group is denoted by	h	E	i	j	h
46	The character of any two irreducible representations of a group are	orthogonal	diagonal	parabola	hyperbola	orthogonal
47	In C_{2v} point group the number of classes are possible	Four	five	six	three	Four
48	In C_{3v} point group the number of classes are possible	Four	five	six	three	Three

49	For the C_{3v} point group, the order of the group is	Four	five	six	three	six
50	Formaldehyde has	Three sigma bonding molecular orbitals	Four sigma bonding molecular orbitals	Five sigma bonding molecular orbitals	Six sigma bonding molecular orbitals	Three sigma bonding molecular orbitals
51	In the C_{2v} point group the 'z' coordinate transformers is	A1	A2	B1	B2	A1
52	The symmetry or antisymmetry is with respect to	Subsidiary axis	Principal axis	Vertical axis	Horizontal axis	Subsidiary axis
53	The single prime and double prime are used to denote	symmetry	chiral	achiral	Mirror image	symmetry
54	Reducible representation is also called as	Total character	Symmetry elements	Symmetry operations	Total elements of symmetry	Total character
55	Irreducible representations reflect the essences of a	Point group	Space group	Symmetry elements	Character table	Point group
56	The C_{2v} point group reducible representations is equal to	$A1+A2+B2$	$2A1 + 2A2+B2$	$A2 +B2$	$A1 +A2$	$2A1 + 2A2+B2$
57	The C_{3v} point group reducible representations is equal to	$A1+A2+B2$	$A1 + 2A2+E$	$A2 +B2$	$A1 +A2$	$A1 + 2A2+E$
58	The T_d point group reducible representations is equal to	$A1+A2+B2$	$A1 + 2E+T2$	$A2 +B2$	$A1 +A2$	$A1 + 2E+T2$
59	To learn more about point groups and the basis of representations it is essential to know all possible	Irreducible representations	Reducible representations	Symmetry elements	Symmetry operations	Irreducible representations
60	In the group theory the letter R indicates	Operation of a group	Symmetry of a group	Order of a group	Class of a group	Operation of a group

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[17CHP103]

KARPAGAM UNIVERSITY
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COIMBATORE-641 021
(For the candidates admitted from 2016 & Onwards)
M.Sc., INTERNAL EXAMINATION-I
CHEMISTRY

PHYSICAL CHEMISTRY-I (Quantum Chemistry and Group Theory)

Time: 2 Hours

Maximum: 50 marks

Date :

PART A

(20 × 1 = 20)

Answer all Questions

1. Black body radiation has a characteristic continuous spectrum of radiation which depends upon
 - a. Body's temperature
 - b. Nature of the body
 - c. Colour of the body
 - d. Density of the body
2. In one dimensional box problem the potential energy of the particle outside the box is
 - a. zero
 - b. unity
 - c. infinity
 - d. fractional
3. The energy levels of the particle in the box are
 - a. quantized
 - b. randomized
 - c. dispersed
 - d. Not-quantized
4. The theory of rigid rotor in space is useful in dealing with
 - a. Rotational spectra of diatomic molecules
 - b. Vibrational spectra of diatomic molecules
 - c. IR spectra of diatomic molecules
 - d. Raman spectra of diatomic molecules
5. In the Hook's law $f = -kx$, k is called
 - a. Force constant
 - b. Gas constant
 - c. Boltzmann constant
 - d. Faraday's constant
6. An one electron system whose potential field is not spherically symmetrical
 - a. Hydrogen atom
 - b. Hydrogen atom in electric field
 - c. Hydrogen molecule
 - d. Helium molecule
7. Which one is Plank equation of protons
 - a. $E = mc^2$
 - b. $E = hv$
 - c. $F = ma$
 - d. $E = ma$
8. If the ψ be a complex function then $\psi^* \psi$ value is
 - a. 0
 - b. 1
 - c. α
 - d. 2
9. A function of X^3 operated by integration with respect to X
 - a. X^6
 - b. $3X^2$
 - c. $X^4/4 + c$
 - d. $k X^3$

10. The two operator is construct a new operator, the operator called as

a. Linear b. Commutator c. Vector d. Laplacian

11. Eigan function and Eigan value represented by

a. First b. Sceond c. Third d. Fourth

12. $\Delta p_x, \Delta x \geq \dots\dots\dots$

a. $4\hbar$ b. 4α c. $\hbar/4\hbar$ d. $\hbar/4\alpha$

13. $\sin 2x$ is not Eigan function of operator d/dx why.....

a. It gives $\cos 2x$ b. It gives $\sin 2x$ c. It gives $\tan 2x$ d. It gives 0

14. Calculate the Eigan value of $\sin 2x$, the operator d^2/dx^2

a. 2 b. 4 c. -4 d. -2

15. Who created the "Gold Foil Experiment?"

a. Dolton b. Lewis c. Bohr d. Rutherford

16. What are the only possible values of the "Spin Quantum Number" in any case?

a. $+1/2$ b. $+1/2$ and $-1/2$ c. 0 d. -1

17. $\psi(x) = A \sin(kx) + \dots\dots\dots$

a. $B \cos(kx)$ b. $B \sec(kx)$ c. $B \sin(kx)$ d. $B \sin(kx)$

18. E results in the allowed energies for a particle in a box

a. $E_n = n^2 \hbar^2 / 8m^2$ b. $E_n = n^2 \hbar^2 / 8ma^2$ c. $E_n = n^2 \hbar^2 / 8m_c 2$ d. $G_n = n^2 \hbar^2 / 4mL^2$

19. The energy level belongs to $E_n = 2n - 1/2$

a. Harmonic oscillator b. Hydrogen atom c. particle in a box d. free particle in motion

20. Which one is de broglie equation

a. $\lambda = h/c$ b. $mv = h/\lambda$ c. $h\nu$ d. $\lambda = h/4\hbar$

PART B

(3 × 2 = 6)

Answer all Questions

21. What is block body radiation? write equation
22. State the uncertainty principle?
23. Write the time depended and independent schrodinger wave equation.

PART C

(3 × 8 = 24)

Answer all Questions

24. a) Explain the postulates of quantum mechanics
(OR)
b) Bohr theory of hydrogen atom with spectrum
25. a) i. Calculate the de Broglie wave length of a body of mass 0.1 kg moving in the a velocity of 1.20×10^3 m/s.
ii. A cricket ball weighing 100g is to be located within 1\AA , what is the uncertainty in its velocity?
(OR)
b) Explain the application of variation method to anharmonic oscillator and Helium atom.
26. a) Set up Schrodinger wave equation for one dimensional harmonic oscillator and solve the equation for its energy and wave equation.
(OR)
b) Derive the Schrodinger equation for rigid rotor.



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DEPARTMENT OF CHEMISTRY
M.Sc., INTERNAL EXAMINATION-I
PHYSICAL CHEMISTRY-I (Quantum Chemistry and Group Theory)
[17CHP103]

Answer Key

PART A

(20 × 1 = 20)

- 1 a. Body's temperature
- 2 c. infinity
- 3 a. quantized
 - a. Rotational spectra of diatomic molecules
- 4 molecules
 - a. Rotational spectra of diatomic molecules
- 5 molecules
- 6 b. Hydrogen atom in electric field
- 7 b. $E = h\nu$
- 8 b. 1
- 9 c. $X^4/4 + c$
- 10 b. Commutator
- 11 d. Fourth
- 12 c. $h/4\pi$
- 13 a. It gives $\cos 2x$
- 14 c. -4
- 15 d. Rutherford
- 16 b. +1/2 and -1/2
- 17 a. $B \cos(kx)$
- 18 b. $E_n = n^2 h^2 / 8ma^2$
- 19 a. Harmonic oscillator
- 20 b. $mv = h/\lambda$

PART B

(3 × 2 = 6 Marks)

21. What is black body radiation? write equation

Answer: A black body is one that absorbs all the EM radiation (light...) that strikes it. To stay in thermal equilibrium, it must emit radiation at the same rate as it absorbs it so a black body also radiates well.

$$E = h\nu$$

22. State the uncertainty principle?

Answer: The Heisenberg uncertainty principle states that it is impossible to find the position and momentum (velocity) of an electron at the same moment. Mathematical representation of this is as follows:

$$\Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

Δx is the uncertainty in position of the electron

Δv_x is the uncertainty in the momentum(velocity)

h = Planck's Constant

m = mass

23. Write the time depended and independent schrodinger wave equation.

Time Depended

$$\psi(\mathbf{r}, t) = \sum_i c_i e^{-iE_i t/\hbar} \psi_i(\mathbf{r})$$

Time In-depended

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

PART C

(3 × 8 = 24 Marks)

24. a) explain the postulates of quantum mechanics

Answer:

1. Associated with any particle moving in a conservative field of force is a wave function which determines everything that can be known about the system.

2. With every physical observable q there is associated an operator Q , which when operating upon the wavefunction associated with a definite value of that observable will yield that value times the wavefunction.
3. Any operator Q associated with a physically measurable property q will be Hermitian.
4. The set of eigenfunctions of operator Q will form a complete set of linearly independent functions.
5. For a system described by a given wavefunction, the expectation value of any property q can be found by performing the expectation value integral with respect to that wavefunction.
6. The time evolution of the wavefunction is given by the time dependent Schrodinger equation.

(OR)

b) Bohr theory of hydrogen atom with spectrum

There was one major objection to the Rutherford model of atom and Bohr was the one to point it out. So while giving his Theory of hydrogen atom, he took the essential features from the Rutherford model of atom but made a change in order to account for the stability of the atom. He made the following postulates: –

- a) An atom consists of a centrally located nucleus having a positive charge and responsible for most of the mass of the atom.
- b) Electrons revolve around with nucleus at centre and in certain fixed circular orbits with definite radius.
- c) The permitted or fixed orbits are such that the angular momentum of an electron is integral multiple of $h/2\pi$, h being the **Planck's constant**.

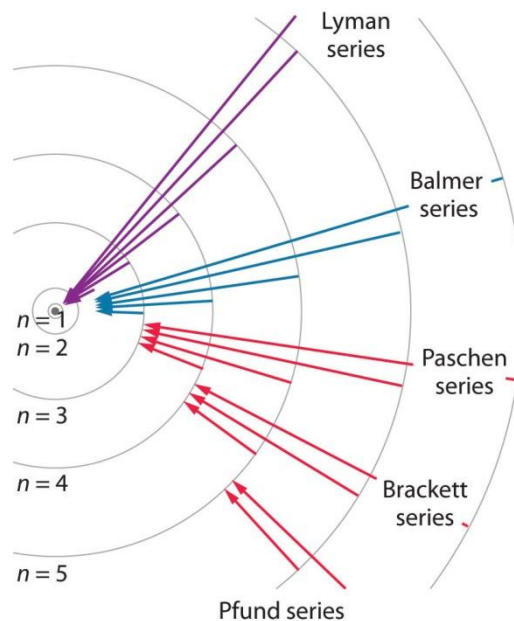
The angular momentum $L = mvr = n(h/2\pi)$, m is the mass of the electron; v is the velocity of the electron in the orbit, n is any integer starting from 1.

n is the principal quantum number. The above equation is known as Bohr quantization postulate.

- d) Electrons do not radiate energy while moving in their permitted orbit. These orbits are called non-radiating or stationary orbits. This is the manner in which Bohr accounted for the stability of the atom.

- e) When an electron jumps from one orbit to another, it absorb/radiate energy. An electron absorbs energy when it jumps from a lower to higher orbit and radiate while jumping from a higher to lower orbit.

Let us assume an electron jumps from orbit n_i to n_f ($n_f > n_i$), then the energy absorbed by the electron is $h\nu = \Delta E = E_f - E_i$, E_f and E_i being the energy of f^{th} and i^{th} orbit respectively.



25. a) i. Calculate the de Broglie wave length of a body of mass 0.1kg moving in the a velocity of 1.20×10^5 m/s.

Solution:

$$\text{de Broglie wave} \quad \lambda = h/mV$$

$$\gg \text{Mass of moving particle } m = 0.1\text{Kg}$$

$$\gg \text{Velocity } V = 1.2 \times 10^5 \text{ m/s and } h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$\lambda = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1} / 0.1\text{Kg} \times 1.2 \times 10^5 \text{ m/s}$$

- ii. A cricket ball weighing 100g is to be located within 1\AA , what is the uncertainty in its velocity?

Answer: $\Delta u \Delta x = h/4\pi m \Delta u \Delta x = h/4\pi m$

$$\Delta u = h/4\pi m \Delta x \Delta u = h/4\pi m \Delta x$$

$$\Rightarrow 6.625 \times 10^{-34} \times 22/7 \times 1 \times 10^{-10} \Rightarrow 6.625 \times 10^{-34} \times 22/7 \times 1 \times 10^{-10}$$

$$\Rightarrow 3.51 \times 10^{-20} \text{ m/s} \Rightarrow 3.51 \times 10^{-20} \text{ m/s}$$

(OR)

- b) Explain the application of variation method to anharmonic oscillator and Helium atom.

Answer: A harmonic oscillator model in four dimensions is presented for the helium atom to estimate the distance to the inner and outer electron from the nucleus, the angle between electrons and the energy levels. The method is algebraic and is not based on the choice of correct trial wave function. Three harmonic oscillators and thus three quantum numbers are sufficient to describe the two-electron system. We derive a simple formula for the energy in the general case and in the special case of the Wannier Ridge. For a set of quantum numbers the distance to the electrons and the angle between the electrons are uniquely determined as the intersection between three surfaces. We show that the excited states converge either towards ionization thresholds or towards extreme parallel or antiparallel states and provide an estimate of the ground state energy.

Hydrogen has been a great laboratory for Quantum Mechanics. After Hydrogen, Helium is the simplest atom we can use to begin to study atomic physics. Helium has two protons in the nucleus ($Z=2$) usually two neutrons ($A=4$) and two electrons bound to the nucleus

26. a) Set up Schrodinger wave equation for one dimensional harmonic oscillator and solve the equation for its energy and wave equation.

Answer: The one-dimensional wave equation is given by

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

In order to specify a wave, the equation is subject to boundary conditions

$$\psi(0, t) = 0 \quad (2)$$

$$\psi(L, t) = 0, \quad (3)$$

and initial conditions

$$\psi(x, 0) = f(x) \quad (4)$$

$$\frac{\partial \psi}{\partial t}(x, 0) = g(x). \quad (5)$$

The one-dimensional wave equation can be solved exactly by [d'Alembert's solution](#), using a [Fourier transform](#) method, or via [separation of variables](#).

d'Alembert devised his solution in 1746, and Euler subsequently expanded the method in 1748. Let

$$\xi \equiv x - vt \quad (6)$$

$$\eta \equiv x + vt. \quad (7)$$

By the [chain rule](#),

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi}{\partial \xi^2} + 2 \frac{\partial^2 \psi}{\partial \xi \partial \eta} + \frac{\partial^2 \psi}{\partial \eta^2} \quad (8)$$

$$\frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2} = \frac{\partial^2 \psi}{\partial \xi^2} - 2 \frac{\partial^2 \psi}{\partial \xi \partial \eta} + \frac{\partial^2 \psi}{\partial \eta^2}. \quad (9)$$

The wave equation then becomes

$$\frac{\partial^2 \psi}{\partial \xi \partial \eta} = 0. \quad (10)$$

Any solution of this equation is [of the form](#)

$$\psi(\xi, \eta) = f(\eta) + g(\xi) = f(x + vt) + g(x - vt), \quad (11)$$

where f and g are *any* functions. They represent two waveforms traveling in opposite directions, f in the [negative \$x\$](#) direction and g in the [positive \$x\$](#) direction.

(OR)

b) Derive the Schrodinger equation for rigid rotor.

Answer: State $|\Psi\rangle|\Psi\rangle$ at $t=0$: $|\Psi(0)\rangle|\Psi(0)\rangle$. The operator (matrix) that governs how it evolves with time will be called $U(t)U(t)$. The state at a later time can then be written

$$|\Psi(t)\rangle=U(t)|\Psi(0)\rangle \quad \Psi(t)=U(t)\Psi(0).$$

The state can be defined to start off *normalized* meaning that it has length one. This has to do with probability and the fact that the total probability over all space is always one. This normalization is written $\langle\Psi(0)|\Psi(0)\rangle=1$ ($\Psi(0)|\Psi(0)\rangle=1$). If the state starts off normalized, we require that it always be normalized because of the conservation of probability.

$$\langle\Psi(t)|\Psi(t)\rangle=\langle\Psi(0)|U^\dagger U|\Psi(0)\rangle=1 \quad \langle\Psi(t)|\Psi(t)\rangle=\langle\Psi(0)|U^\dagger U|\Psi(0)\rangle=1$$

Because $\langle\Psi(0)|\Psi(0)\rangle=1$ ($\Psi(0)|\Psi(0)\rangle=1$), that means that $U^\dagger U=IU^\dagger U=I$ where I is the identity matrix. This type of operator is called a *unitary operator*. Time translation is represented by a unitary operator: $U(t)U(t)$.

After no time has passed a system must be in the same state it was in so when you act on the state with $U(0)U(0)$ you must get the same state. This means that $U(0)=IU(0)=I$ because acting on a state with the identity operator will give the same state.

After a tiny bit of time ϵ has passed, U must be very close to I so you can write $U(\epsilon)=I-i\hbar H\epsilon$ ($U(\epsilon)=I-i\hbar H\epsilon$). $i\hbar$ is just a constant with historical significance and H is some operator with ϵ just being the tiny bit of elapsed time.

Remembering that $U^\dagger U=IU^\dagger U=I$, you can plug in U and it's hermitian conjugate U^\dagger .

$$U^\dagger U=(I+i\hbar H^\dagger \epsilon)U^\dagger U=(I+i\hbar H^\dagger \epsilon)(I-i\hbar H\epsilon)=(I-i\hbar H\epsilon)=I$$

Distributing, disregarding the term of order ϵ^2 , and noting that $I^2=II^2=I$ (just like one squared equals one) you find that $H=H^\dagger H=H^\dagger$. This type of operator is called a *hermitian operator*. Hermitian operators represent observables. In the case of H , the observable you observe is a system's energy.

Let's let U act on some state ψ and find the difference between $U(\epsilon)U(\epsilon)$ and $U(0)U(0)$.

$$(U(\epsilon)-U(0))\psi=-i\hbar H\psi \quad (U(\epsilon)-U(0))\psi=-i\hbar H\psi.$$

If you divide by ϵ and let epsilon tend to zero you get the limit definition of a derivative in time! You are left with

$$\partial\psi/\partial t=-i\hbar H\psi \quad \partial\psi/\partial t=-i\hbar H\psi.$$

You have the time-dependent Schrödinger equation!

*****All the Best*****

Reg. No.....

[17CHP103]

KARPAGAM UNIVERSITY
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COIMBATORE-641 021
(For the candidates admitted from 2017 & Onwards)
M.Sc., DEGREE INTERNAL EXAMINATION

CHEMISTRY
PHYSICAL CHEMISTRY-I (Quantum Chemistry and Group Theory)
INTERNAL II

Time: 2 Hours

Maximum: 50 marks

Date:

PART A
Answer all Questions

(20 × 1 = 20)

- The water molecule belongs to the group
a. C_{6v} b. C_v c. C_{2v} d. C_{3v}
- The benzene molecule (C_6H_6) has how many vibrational modes
a. 6 b. 12 c. 24 d. 30
- The method applicable for a system which wave functions may be guessed
a. Perturbation method b. Variation method
c. Normalization of the wave function d. Making the wave functions orthogonal
- Write the energy level for the free particle in motion
a. $E_n = 2n - 1/2$ b. $E_n = n^2$ c. E_n is continuous d. $E_n \propto n^2$
- The shape of $BeCl_2$ molecules is
a. Linear b. Triangular planar c. Tetrahedral d. octahedral
- For the symmetry operation "rotation" the corresponding symmetry element is
a. Identity element b. Plane of symmetry
c. Centre of symmetry d. Proper axis of symmetry
- For the symmetry operation "reflection" the corresponding symmetry element is
a. Identity element b. Plane of symmetry
c. Centre of symmetry d. Proper axis of symmetry
- An array of numbers arranged in rows and columns are called
a. Matrices b. determinants c. Space lattices d. Miller indices
- The Carbon-di-oxide (CO_2) has how many vibrational modes
a. 3 b. 8 c. 4 d. 6
- The molecule with C_{3v} point group
a. acetylene b. water c. ammonia d. Boron trichloride

- For a pyramidal molecule with point group C_{3v} , the number of theoretically predicted IR fundamental bands
a. Three b. Four c. Five d. Six
 - For chloro trifluoride molecule the number of observed Raman bands and IR bands are four each, the predicted geometry is
a. Pyramidal b. planar c. T-shaped d. bent
 - In case of molecules with a centre of symmetry the vibrational modes are anti-symmetric to centre of inversion are
a. IR inactive b. IR active c. Raman inactive d. Raman hyper active
 - For Raman activity the vibrations should involve a change in
a. polarizability b. magnetization c. Magnetic susceptibility d. Surface tension
 - A diatomic vibrating molecule can be represented by a simple model called
a. Simple harmonic oscillator b. Rigid rotor
c. Particle in one dimensional box d. Particle in three dimensional box
 - The quantum number 'm' is called
a. Principal quantum number b. Azimuthal quantum number
c. Magnetic quantum number d. Angular momentum quantum number
 - The basic theorem is concerned with the elements of the matrices constituting the irreducible representation of a group is called
a. Faradays theorem b. The great orthogonality theorem
c. Normalized theorem d. Van der Waals theorem
 - Character tables are constructed using
a. Symmetry elements b. Orthogonality theorem
c. Symmetry operations d. Irreducible operations
 - The corresponding matrix for the operation E is
a. Zero matrix b. Square matrix c. Diagonal matrix d. Unit matrix
 - Reducible representation is also called as
a. Total character b. Symmetry elements
c. Symmetry operations d. Total elements of symmetry
- PART-B**
Answer all Questions
- (3 × 2 = 6 Marks)
- State the mutual exclusion principle?
 - What is meant by a improper rotation of symmetry?
 - What are the matrix notation for σ and S_n ?

PART-C
Answer all Questions

(3 × 8 = 24 Marks)

24. (a) (i) Define Symmetry elements.
(ii) Write notes on symmetry operations with examples.
(OR)
(b) (i) Distinguish between vertical plane and horizontal plane symmetry.
(ii) Construct the multiplication table for a C_{2v} point group?
25. (a) (i) Write on reducible and irreducible representation of the group.
(ii) What are the rules to be followed to identify a point group?
(OR)
(b) (i) State and explain the great orthogonality theorem.
(ii) How will you construct the multiplication table for a C_{3v} point group?
26. (a) (i) What is meant by zeropoint energy?
(ii) Explain the application of variation method to anharmonic oscillator atom.
(OR)
(b) (i) Define abelian and cyclic groups. Prove the statement, every cyclic group is abelian but the converse is not true.
(ii) Explain the symmetry selection rules for infra-red and Raman spectra.



KARPAGAM ACADEMY OF HIGHER EDUCATION

(Under Section 3 of UGC Act 1956)

COIMBATORE-641 021

M.Sc., DEGREE INTERNAL EXAMINATION-2017

CHEMISTRY

PHYSICAL CHEMISTRY-I (Quantum Chemistry and Group Theory)

[17CHP103]

INTERNAL II

Time: 2 Hours

Maximum:50 marks

Answer Key

PART A

(20 x 1 =20)

1. c. C_2V
2. d. 30
3. b. Variation method
4. c. En is Continuers
5. a. Linear
6. d. Proper Axis of Symmetry
7. b. Plane of symmetry
8. a. Matrices
9. c. 4
10. c. ammonia
11. a. Three
12. c. T-shaped
13. b. IR active
14. a. polarizability
15. a. Simple harmonic oscillator
16. c. Magnetic quantum Numbers
17. b. The great orthogonality theorem
18. b. orthogonality theorem
19. d. Unit matrix
20. a. Total character

PART-B

(3x2 = 6 Marks)

21. State the mutual exclusion principle

Answer: In molecular spectroscopy, the rule of mutual exclusion states that no normal modes can be both Infrared and Raman active in a molecule that possesses a centre of symmetry. This is a powerful application of group theory to vibrational spectroscopy, and allows one to easily detect the presence of this symmetry element by comparison of the IR and Raman spectra generated by the same molecule

22. What is meant by a improper rotation of symmetry

Answer: This is a compound operation combining a rotation (C_n) with a reflection through a plane perpendicular to the C_n axis σ_h . (C_n followed by σ_h) $\sigma C_n = S_n$

23. What is the matrix notation for σ and S_n .

Answer: Sigma notation is used as a shorthand way of writing sums. If a vector X (either a row or column vector) has N components, then alternative notations are used when we want to be explicit about the index over which the summation is performed or the number of elements of the vector.

$$X = \begin{bmatrix} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{bmatrix}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

PART-C

(3 x 8 = 24 Marks)

23. (a) (i) Define Symmetry elements and Symmetry Operation

Answer: Operations which leave an object looking the same are called **symmetry operations**. This term is confined to operations where there is definitely no difference in the appearance of a molecule before and after performing the operation.

A classification of molecules is done with reference to five symmetry operations. A symmetry operation is characterized by a point, a straight line or a plane as symmetry element. Thus, any symmetry element is connected with one or more symmetry operations that yield an image identical to the original molecule.

Identity E is a symmetry operation without effect, e.g. a rotation with an angle of 360° . Though such an operation seems useless, it is of importance in group theory as any group needs to have one neutral element, i.e. identity. Furthermore, this symmetry operation is the base for the classification of asymmetric molecules like CHBrClF which have no other symmetry.

An **n-fold rotation** denotes a rotation through an angle of $360^\circ/n$, thereby yielding an image indistinguishable from the original. The n-fold axis C_n is the respective symmetry element.

In inversion, any point of an object is taken, moved through a centre of inversion (i.e. the symmetry element i) and placed in equal distance beyond this centre.

Reflection moves any point of the original orthogonally to a point beyond some reflection plane or mirror plane. This plane is the respective symmetry element σ .

A **rotary reflection** around some rotary reflection axis S_n (i.e. symmetry element) combines an rotation through $360^\circ/n$ followed by reflection on a horizontal plane.

(OR)

(b). (i) Distinguish between vertical plane and horizontal plane symmetry.

Answer:

Reflection: σ (the symmetry element is called a mirror plane or plane of symmetry)

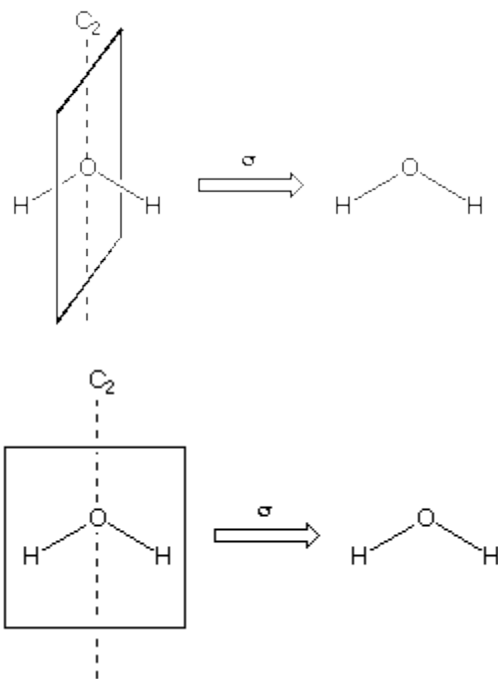
If reflection about a mirror plane gives the same molecule/object back then there is a plane of symmetry (σ).

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 (s_d)

H_2O posses 2 s_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: s_v

XeF_4 has two planes of symmetry parallel to the principle rotation axis and bisecting the angle between 2 C_2 axes : s_d

ii) Construct the multiplication table for a C_{2v} Point group

Answer: C_{2v} Character Table

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
II		I			III	IV

On the left corner of the character table, the point group is shown. Any character table has four main areas, I, II, III and IV.

Area I consists of the characters of the irreducible representations of the group.

1. Symbols A and B are given to one dimensional representation, E to two dimensional representation, and T to three dimensional representation.
2. When a one dimensional representation is symmetric with respect to $/n$ about the principal C_n axis, i.e., $\chi(C_n) = 1$, symbol A is π rotation by 2 given and B is given, if it is antisymmetric, $\chi(C_n) = -1$.
3. Subscripts 1 is attached to A and B, if the operation is symmetric to C_2 perpendicular to the principal axis. and subscript 2 is attached if it is antisymmetric .
4. Prime is attached to all letters, (A', B', etc.) if the operation is symmetric h plane. Double prime is attached (A'', B'', etc.) if it is σ with respect to antisymmetric.
5. If a group has centre of inversion, then subscript 'g' is used if it is symmetric with respect to inversion and subscript 'u' is used if it is antisymmetric with respect to inversion.

Area III consists of symbols x, y, z, R_x , R_y , and R_z . These represent the Cartesian coordinates and the rotations about the three axes. If two symbols are placed within parentheses, [ex: (x,y), (R_x , R_y)], it means that both put together form the basis and they cannot be separated. Area IV contains the squares and binary products of the coordinates

25. (a) (i) Write on different between reducible and irreducible representation of the group.

Answer:

A reducible representation (ρ, V) has at least one sub representation (ρ_W, W) where W a subset of V and W is closed under the action of ρ .

Completely reducible means that there are subsets W_i of V such that each W_i forms together with its ρW_i a sub representation and $V = \bigoplus W_i$.

As @Derek Holt mentioned in the comments a counterexample to your statement that every reducible representation can be written as a direct sum of irreducible is the following:

$$x \mapsto (10x1) \quad x \mapsto (1x01)$$

You can check that
 $a(10)a(10)$

, where a is a real number is an irreducible sub representation but $(10x1)(1x01)$ cannot be written as a direct sum of irreducible sub representations because it is not diagonalizable ($\det=1$).

(ii) What are the rules to be followed to identify a point group.

Answer: Identification of molecular point groups:

The whole molecules are divided into three broad categories.

Molecules of low symmetry

- Molecules of high symmetry
- Molecules of special symmetry.

Molecules of Low Symmetry

The starting point could be the molecules containing no symmetry elements other than E, such molecules are unsymmetrically substituted and these molecules are said to belong to C_1 point group.

The TeCl_2Br_2 molecules with its structure in gaseous phase belongs to C_1 point group, and tetrahedral carbon and silicon compounds of the formula AHFCIBr ($\text{A}=\text{C}, \text{Si}$).

Molecules of High Symmetry

In this category all the molecules containing C_n axis (invariably in the absence or presence of several other types of symmetry of elements) are considered. There are three main types of point groups C_n , D_n , and S_n .

Molecules of special Symmetry

This class has two groups of molecules:

- Linear or infinite groups and
- Groups which contain multiple higher-order axes.

(OR)

(b) (i) State and explain the great orthogonality theorem.

Answer: Great Orthogonality Theorem:

The matrices of the different Irreducible Representations (IR) possess certain well defined interrelationships and properties. Orthogonality theorem is concerned with the elements of the matrices which constitute the IR of a group.

The mathematical statement of this theorem is,

$$\sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)'m'n']^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$$

Where,

i, j – Irreducible Representations

l_i, l_j – Its dimensions

h – Order of a group

$\Gamma_i(R)_{mn}$ – Element of m^{th} row, n^{th} column of an i^{th} representation

$\Gamma_j(R)'m'n'$ – Element of m'^{th} row, n'^{th} column of j'^{th} representation

$\delta_{ij} \delta_{mm'} \delta_{nn'}$ – Kronecker delta

Kronecker delta can have values 0 and 1. Depending on that the main theorem can be made into three similar equations.

i.e.,

1. When, $\Gamma_i \neq \Gamma_j$ and $j \neq i$, then $\delta_{ij} = 0$

$$\text{Therefore, } \sum_R [\Gamma_i(R)_{mn}] [\Gamma_j(R)'m'n']^* = 0$$

2. When, $\Gamma_i = \Gamma_j$ and $j = i$, then $\delta_{ij} = 1$

$$\text{Therefore, } \sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)'m'n']^* = 0$$

From these two equations we can say the Orthogonality theorem as, “the sum of the product of the irreducible representation is equal to zero”.

3. When $i = j$, $m = m'$, $n = n'$

$$\text{Then, } \sum_R [\Gamma_i(R)_{mn}] [\Gamma_i(R)_{mn}]^* = \frac{h}{l_i}$$

From the above equations some important rules of the irreducible representations of a group and there character were obtained.

(ii) How will you construct the multiplication table for C_{3v} point group

Answer: Character Table for C_{3v} Point Group:

1. For C_{3v} point group, there are 6 symmetry operations and 3 classes, i.e., $\Gamma_1, \Gamma_2, \Gamma_3$.

2. The sum of the squares of the dimensions of the symmetry operations = 6.

$$\text{i.e., } l_1^2 + l_2^2 + l_3^2 = h = 6.$$

This can only be satisfied by, 2 one dimensional and 1 two dimensional representations.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	a_1	b_1
Γ_2	1	a_2	b_2
Γ_3	2	a_3	b_3

3. The sum of the dimensions of Γ_1 also 6.

Therefore, its characters are (1 1 1).

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	a_2	b_2
Γ_3	2	a_3	b_3

4. All operations must satisfy the orthogonality condition, $\sum_R \Gamma_i(R) \Gamma_j(R) = 0$

i.e., For $\Gamma_1 \cdot \Gamma_2$

$$\text{i.e., } 1 \cdot 1 + 2 \cdot a_2 \cdot 1 + 3 \cdot b_2 \cdot 1 = 0$$

Let $a_2 = 1$ and $b_2 = -1$

Then $\Gamma_1 \cdot \Gamma_2 = 0$

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	a_3	b_3

i.e., For $\Gamma_3 \cdot \Gamma_2$

i.e., $2 \cdot 1 + 2 \cdot a_3 \cdot 1 - 3 \cdot b_3 \cdot 1 = 0$

Let $a_3 = -1$ and $b_3 = 0$

Then $\Gamma_3 \cdot \Gamma_2 = 0$

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

For any character table there are 4 areas.

For Area I:

Assign the Mullicon symbols.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
B	2	-1	0

For Area III:

In order to assign the Cartesian coordinates different operations are performed on each of the axes. Here we were finding the symbols X, Y, Z represents coordinates and rotations R_x , R_y and R_z .

26. (a).(i) What is meant by zeropoint energy?

Answer: Zero-point energy (ZPE) or ground state energy is the lowest possible energy that a quantum mechanical system may have. Unlike in classical mechanics, quantum systems constantly fluctuate in their lowest energy state due to the Heisenberg uncertainty principle.

In classical mechanics all particles can be thought of as having some energy made up of their potential energy and kinetic energy. Temperature, for example, arises from the intensity of random particle motion caused by kinetic energy (known as brownian motion). As temperature is reduced to absolute zero, it might be thought that all motion ceases and particles come completely to rest. In fact, however, kinetic energy is retained by particles even at the lowest possible temperature. The random motion corresponding to this zero-point energy never vanishes as a consequence of the uncertainty principle of quantum mechanics.

(ii). Explain the application of variation method to anharmonic oscillator atom.

Answer: The *harmonic oscillator* is based on Hooke's law and the idea of perpetual conversion of kinetic into potential energy and vice versa. In practice, this description is only an adequate approximation of e.g. a chemical bond in the limit of very small oscillations. The *anharmonic oscillator* model addresses that by adding higher-order terms of the elongation x to account for deviations farther away from $x=0$. These extra terms are a *perturbation* of the Hamiltonian for the harmonic oscillator:

where the red parts represent the perturbation.

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4$$

Knowing the wave function of the harmonic oscillator and its eigenvalues, we can calculate the anharmonic energy corrections by applying the perturbation Hamiltonian, H_1 to the unperturbed wave function of the harmonic oscillator.

(OR)

(b).(i) Define abelian and cyclic groups. Prove the statement. Every cyclic group is abelian but the converse is not true.

Answer: For finite cyclic groups this is a very valid proof. The only addendum is the infinite cyclic group \mathbb{Z} . Of course, it can be proved directly (below) but, the proof you provide is much more revealing to the structure of abelian groups.

Now, consider $x, y \in G, x, y \in G$ where G is cyclic. Since G is cyclic, it is generated by some element, say a . Then $xy = (a^m)(a^n)xy = (a^m)(a^n)$ for some $m, n \in \mathbb{Z}$. Writing out this product, using the associativity, and then recollecting terms by definition of powers we see $xy = a^{m+n}xy = a^{m+n}$. Similarly, $yx = a^{m+n}yx = a^{m+n}$ so that G is abelian.

Consider $n = 9$. Then, since 3 is not relatively prime to itself, $\mathbb{Z}/3 \times \mathbb{Z}/3$ is not cyclic, so we see that not every group of order 9 is cyclic and not every abelian group of order 9 is cyclic. Since these are the only abelian groups of order 9 and we know that groups of order p^2 for a prime p are abelian, this comprises the entire set of groups of order 9, so we can say that every group of order 9 is abelian.

(ii) Explain the symmetry selection rules for infra-red and Raman spectra.

Answer: The **selection rule** says, that vibrations are only IR active (or allowed), if the molecular dipole moment changes during the vibration. A diatomic molecule with the same atoms cannot be excited to vibrate because no dipole moment is present. In contrast, molecules with various types of atoms can interact with incident radiation, and even if a dipole moment is not present in the beginning it can be induced due to antisymmetric displacement of the center of charge (e.g., CO_2).

A molecule of n atoms has $3N$ degrees of freedom. In a non-linear molecule 3 of these are rotational and 3 of these degrees are translational, and the remaining belong to fundamental vibrations (normal modes). In a linear molecule 2 degrees are rotational and 3 degrees are translational. The number of fundamental vibrations in a non-linear molecule is therefore **$3N-6$** and in a linear molecule it is **$3N-5$** . The water molecule is an example for a non-linear molecule and has 3 fundamental vibrations ($3 \times 3 - 6$). The CO_2 molecule is an example for a linear molecule and has 4 fundamental vibrations ($3 \times 3 - 5$).

*****All the Best*****

KARPAGAM UNIVERSITY

Karpagam Academy of Higher Education
(Established Under Section 3 of UGC Act 1956)

COIMBATORE – 641 021

(For the candidates admitted from 2015 onwards)

M.Sc., DEGREE EXAMINATION, NOVEMBER 2015

First Semester

CHEMISTRY**PHYSICAL CHEMISTRY I**

(Quantum Chemistry and Group Theory)

Time: 3 hours

Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)

(Question Nos. 1 to 20 Online Examinations)

(Part - B & C 2 ½ Hours)

PART B (5 x 6 = 30 Marks)

Answer ALL the Questions

21. (a) (i) Give an explanatory note on time dependent Schrodinger equation.
(ii) S.T. Weins and Rayleigh Jeans law are the limiting cases of plancks expression.

Or

- (b) i) Write a note on operator
ii) Give a detailed account on Hamiltonian operators.

22. (a) Compare the classical mechanics and quantum mechanics with particle in three dimensional box.

Or

- (b) Solving of Schrodinger equation for one-dimensional harmonic oscillator

23. (a) Give an account on perturbation theory and its application to He atom.

Or

- (b) (i) Explain radial distribution functions.
(ii) Explain the perturbation method to anharmonic oscillator.

24. (a) i) What is a group?
ii) What are the cyclic, finite and infinite group's?
iii) Define class.

Or

- (b) i) Define matrix?
ii) Write a note on square, diagonal, null matrix?

25. (a) (i) What are the relationships between reducible and irreducible representation of the group.

- (ii) What are the Properties of irreducible representation?

Or

- (b) Explain the symmetry selection rules for infra-red and Raman spectra.

PART C (1 x 10 = 10 Marks)

(Compulsory)

26. Give an detail account of black body radiation?

Reg. No.....

[14CHP103]

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(For the candidates admitted from 2014 onwards)

M.Sc. DEGREE EXAMINATION, NOVEMBER 2014

First Semester

CHEMISTRY

PHYSICAL CHEMISTRY – I

(Quantum Chemistry and Group Theory)

Time: 3 hours

Maximum : 60 marks

PART – A (10 x 2 = 20 Marks)

Answer any TEN Questions

1. How will you prove light is a wave?
2. Define commutator operator and give one example.
3. What are Eigen values and Eigen functions and give suitable examples.
4. What is meant by normalization of wave functions?
5. State Schrodinger wave equation for a particle in a three dimensional box and rigid rotor.
6. What do the two spherical polar coordinates θ and ϕ measure.
7. Derive the equation for approximation method to helium atom.
8. Define variation principle.
9. State the equation for perturbation method to helium atom.
10. What are the differences between proper and improper notations?
11. Prove that $C_2(x) C_2(y) = C_2(z)$.
12. What are sub-groups? Give one suitable example.
13. Explain the symmetry selection rule for IR.
14. Find out the class and order of a group for C_{2v} and C_{3v} point groups.
15. What is meant by mutual exclusion principle?

PART B (5 X 8= 40 Marks)

Answer ALL the Questions

16. (a) Set up Schrodinger wave equation for the rigid rotor of diatomic molecule.
Or
(b) Set up Schrodinger wave equation for one dimensional box and solve the equation for its energy and wave equation.

17. (a) What are the applications of perturbation method to anharmonic oscillator and Helium atom.

Or

- (b) Derive Schrodinger equation for H-atom.

18. (a) (i) Define class and sub-group.
(ii) Write notes on similarity transformation.
(iii) Show that the element $[1, -1, i, -i]$ form a group.

Or

- (b) (i) Prove the following:
 $S_4^4 = E, S_3^3 = \sigma_h, S_5^4 = C_5^4, S_4^2 = C_2$
(ii) Distinguish between vertical plane and horizontal plane.
(iii) Prove that $C_2(x) C_2(y) = C_2(z)$.

19. (a) (i) What are the relationship between reducible and irreducible representation of the group.

- (ii) What are the properties of irreducible representation?

Or

- (b) (i) State and explain the great orthogonality theorem.
(ii) How will you construct the character table for a C_{2v} and C_{3v} point group using the great orthogonality theorem?

20. Compulsory : -

What are the postulates of Quantum mechanics?
