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M.Sc. CHEMSITY
COURSE MATERIALS
PHYSICAL CHEMISTRY – II
SCHP32

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UNIT -1

Wave–Particle Duality

The concept of wave–particle duality is a fundamental idea in quantum mechanics which states that every particle or quantum entity, such as an electron or photon, exhibits both wave-like and particle-like properties. This dual nature was first observed in light, which could behave like a wave in interference and diffraction experiments, and like a particle in the photoelectric effect. Later, experiments showed that even electrons and atoms could produce wave patterns under suitable conditions. This discovery broke away from classical physics, which separated matter and energy into distinct categories. Wave–particle duality implies that particles like electrons have wavelengths, and their behavior can be predicted by wave equations. This concept is key to understanding atomic and molecular structure, electron motion, and the development of quantum theory. It reveals the complex and probabilistic nature of microscopic particles and underlines the limitations of classical mechanics at small scales.

Uncertainty Principle

The uncertainty principle is a core concept of quantum mechanics formulated by Werner Heisenberg. It states that it is impossible to simultaneously determine both the exact position and momentum of a particle with absolute precision. The more accurately one of these quantities is known, the less accurately the other can be measured. This is not due to experimental limitations but a fundamental property of nature at the quantum level. The uncertainty principle reflects the wave-like nature of particles, as waves are spread out and not localized. This principle has profound implications, such as the impossibility of defining exact electron orbits in atoms, as suggested by classical physics. Instead, electrons exist in regions of probability called orbitals. The uncertainty principle challenges the idea of deterministic behavior in physical systems and replaces it with a probabilistic model of the universe at atomic and subatomic scales.

Particle Wave and Schrödinger Wave Equation

In quantum mechanics, particles such as electrons are not just small hard spheres but exhibit wave-like properties, described by a mathematical function known as a wave function. The Schrödinger wave equation is a key tool that governs the behavior of these quantum particles. This equation treats particles as waves and helps predict their probable locations and energies. It provides a quantitative way to understand atomic structure, chemical bonding, and reactions. Unlike classical mechanics, which gives exact outcomes, the Schrödinger equation gives a set of probable results. When solved for systems like hydrogen atoms, it gives energy levels that match experimental observations. The equation has both time-dependent and time-independent forms. It plays a vital role in all areas of chemistry and physics where wave-like behavior of particles needs to be considered.

Wave Function and Properties of Wave Function

The wave function is a mathematical expression that describes the quantum state of a particle or system of particles. It contains all the information about the system, including the probability of finding the particle at a certain position and time. Though the wave function itself may not have physical meaning, its square gives the probability density. Important properties of a valid wave function include continuity, single-valuedness, and finite value at all points. It must also be normalizable, meaning its total probability over all space should be one. The shape of the wave function changes with different energy levels and potential fields. In chemistry, wave functions are crucial for understanding molecular orbitals and electronic structures of atoms. Their interpretation lies at the heart of quantum mechanics and modern theoretical chemistry.

Normalized, Orthogonal, Orthonormal Functions

In quantum mechanics, wave functions must follow certain mathematical conditions to represent physical systems accurately. A wave function is said to be normalized when the total probability of finding the particle somewhere in space is equal to one. This ensures that the wave function reflects a real, observable particle. Two wave functions are orthogonal if the integral of their product over all space is zero. This means they represent distinct quantum states that do not interfere with each other. If wave functions are both normalized and orthogonal, they are called orthonormal. Orthonormal sets are useful in building complete bases for quantum systems, much like a coordinate system. These properties help in solving quantum problems systematically and ensure consistency in predictions made by the Schrödinger equation.

Eigen functions, Hermitian properties of operators

In quantum mechanics, physical observables like position, momentum, and energy are represented by operators. When an operator acts on a function and simply multiplies it by a constant, that function is called an eigenfunction, and the constant is the corresponding eigenvalue. For example, if $\check{A}\psi=a\psi$, then ψ is an eigenfunction of operator $\check{A}$ and a is the eigenvalue. Eigenfunctions describe states that have definite values (eigenvalues) for the physical quantity. These concepts are key to solving quantum systems.

Operators used in quantum mechanics are usually Hermitian. A Hermitian operator has the property that the integral of one function times the operator acting on another is equal to the reverse. Mathematically, this ensures that all eigenvalues are real, which is essential because physical quantities like energy and momentum must be real. Hermitian operators also have orthogonal eigenfunctions, meaning different eigenfunctions of the same operator are mathematically independent.

Introduction to quantum mechanics-black body radiation

Quantum mechanics originated from the failure of classical physics to explain certain phenomena. One major issue was black body radiation. A black body is an idealized object that absorbs all incident radiation and re-emits it in a characteristic spectrum. According to classical physics (Rayleigh-Jeans law), the energy radiated at high frequencies should be infinite—this contradiction is called the ultraviolet catastrophe.

Experiments showed that energy emitted by black bodies peaked at certain wavelengths and did not diverge. In 1900, Max Planck proposed that energy is not continuous but quantized. He suggested that electromagnetic energy could only be emitted or absorbed in discrete amounts called quanta or photons. The energy of each quantum is proportional to the frequency of radiation, given by $E=h\nu$, where h is Planck's constant.

This idea marked the birth of quantum theory. Planck's explanation matched experimental results and resolved the ultraviolet catastrophe. It introduced the revolutionary concept that energy levels are discrete, not continuous. This formed the foundation for further quantum developments, including the photoelectric effect, atomic models, and Schrödinger's equation.

Photoelectric Effect

The photoelectric effect refers to the emission of electrons from a metal surface when light shines on it. Classical physics expected that light of any intensity would eventually cause electron ejection, and that higher intensity would release more energy. However, experiments showed that electrons were only emitted if the light had a minimum frequency, regardless of intensity. This contradicted classical wave theory.

In 1905, Albert Einstein explained this by proposing that light is made up of discrete particles called photons. Each photon has energy $E=h\nu$, where h is Planck's constant and ν is the frequency of the light. If the photon energy is greater than the metal's work function (the minimum energy needed to release an electron), the excess energy is transferred to the electron as kinetic energy.

Einstein's theory explained why no electrons were emitted below a threshold frequency and why increasing light intensity (without increasing frequency) had no effect. The photoelectric effect proved the particle nature of light and confirmed the concept of quantization of energy.

This effect supported the idea that light has both wave and particle characteristics, known as wave-particle duality. Einstein received the Nobel Prize in Physics in 1921 for this explanation, which became a cornerstone of quantum mechanics.

Hydrogen Spectrum

The hydrogen atom emits light at specific wavelengths when electrons move between energy levels. When an electron absorbs energy, it jumps to a higher energy level. When it returns to a lower level, it emits energy as light. These emitted lights appear as spectral lines. The hydrogen spectrum is the pattern of these lines and is unique to hydrogen.

In the 1880s, Balmer found an empirical formula for visible lines in hydrogen. Later, Rydberg extended it to other series (Lyman, Paschen, etc.) in different regions of the spectrum. However, classical physics couldn't explain why only certain energy levels or wavelengths appeared.

In 1913, Niels Bohr proposed a quantum model of the hydrogen atom. He suggested that electrons orbit the nucleus in specific, quantized orbits. Only certain energy levels are allowed, and transitions between these levels result in the emission or absorption of photons with energy equal to the difference between the levels.

Bohr's model successfully explained the hydrogen spectrum and calculated its line positions accurately. The energy levels were given by the formula $En=-13.6\ eV/n^2$, where n is a positive integer. The hydrogen spectrum thus provided strong evidence for quantized energy states and laid the groundwork for the development of quantum atomic models.

Need for Quantum Mechanics

Classical mechanics, developed by Newton, could accurately explain the motion of planets, falling objects, and machines. However, it failed at atomic and subatomic scales. Phenomena like black body radiation, photoelectric effect, hydrogen atom spectrum, and electron diffraction could not be explained using classical theories. In the early 20th century, experiments showed that particles like electrons also exhibit wave-like behavior, and that light, normally seen as a wave, also behaves like a stream of particles. These dualities couldn't be understood with classical laws. Additionally, the concept of determinism in classical physics—where future states could be exactly predicted—didn't hold true for particles at quantum scales. Instead, probabilities and uncertainties dominate. This led to the birth of quantum mechanics, a theory designed to explain the behavior of matter and energy at very small scales. It introduced new ideas such as quantization of energy, wave functions, and operators.

Quantum mechanics was not just a correction—it was a fundamental shift in how scientists viewed nature. It became essential for understanding atoms, molecules, chemical bonding, semiconductors, lasers, and even biological processes.

Postulates of Quantum Mechanics

Quantum mechanics is based on a few key postulates that form its mathematical and conceptual foundation. These postulates differ greatly from classical physics and are essential for describing microscopic systems.

Postulate 1: The state of a quantum system is completely described by a wave function. This function contains all the information about the system.

Postulate 2: Every observable physical quantity (like energy, momentum, position) is represented by a mathematical operator.

Postulate 3: When an observable is measured, the only possible outcomes are the eigenvalues of the corresponding operator.

Postulate 4: The probability of getting a specific result in a measurement is given by the square of the wave function's magnitude.

Postulate 5: The time evolution of the wave function is determined by the Schrödinger equation.

These postulates introduce core ideas such as uncertainty, superposition, and quantization, which don't appear in classical mechanics. They allow predictions about atoms, light-matter interactions, and chemical reactions, and are verified by countless experiments.

Schrödinger Wave Equation

The Schrödinger equation is the central equation of quantum mechanics. It describes how the wave function of a system evolves in space and time. Unlike classical equations, it doesn't give exact particle paths but instead gives a probability wave. Proposed by Erwin Schrödinger in 1926, the equation treats particles like electrons as waves. Solving this equation gives the wave function, which contains information about the particle's position, energy, and behavior.

The wave function is a complex-valued function whose square gives the probability density. The Schrödinger equation allows prediction of the behavior of electrons in atoms, molecules, and solids. It successfully explained the hydrogen atom spectrum, chemical bonding, and tunneling phenomena. It applies to all quantum systems, from particles in a box to molecular orbitals. The equation is used in both time-dependent and time-independent forms, depending on whether the system changes with time or remains in a steady state.

This equation replaced Newton's laws at the atomic level and is a cornerstone of modern physics and chemistry.

Time-Independent Schrödinger Equation

The time-independent Schrödinger equation is used when a quantum system does not change with time, such as an electron in a fixed atomic potential. In such cases, the system is in a stationary state, meaning the energy remains constant over time. This form of the equation focuses on solving for the energy levels and wave functions of quantum systems. It is often used in problems like the hydrogen atom, particle in a box, quantum harmonic oscillator, and molecular orbitals. Solving this equation gives eigenfunctions (the allowed wave functions) and eigenvalues (the corresponding energy levels). These energy levels are quantized, meaning only certain discrete values are allowed. The time-independent equation helps explain phenomena like atomic spectra, molecular vibrations, and chemical bonding. It allows us to calculate how electrons are distributed in atoms and molecules. It’s widely used in quantum chemistry, solid-state physics, and nanotechnology. Though it doesn’t include time evolution, it gives crucial insight into the structure and stability of matter at microscopic scales.

Time-Dependent Schrödinger Equation

The time-dependent Schrödinger equation describes how a quantum system’s wave function changes over time. It is more general than the time-independent version and applies to systems where the potential or state changes with time.

This equation governs the dynamics of quantum particles, meaning how their probability distributions evolve. It helps in understanding how particles move, interact, or transition between states. In this case, the wave function depends on both position and time, and solving the equation gives the system’s behavior at any moment. It is key in problems like quantum transitions, interference, and quantum computing. It plays an important role in quantum optics, spectroscopy, and the design of lasers and semiconductors. It also describes how systems evolve from one stationary state to another. The time-dependent equation introduces concepts like superposition, wave packet motion, and quantum coherence. It reflects the probabilistic nature of quantum systems and allows predictions of future behavior based on initial conditions.

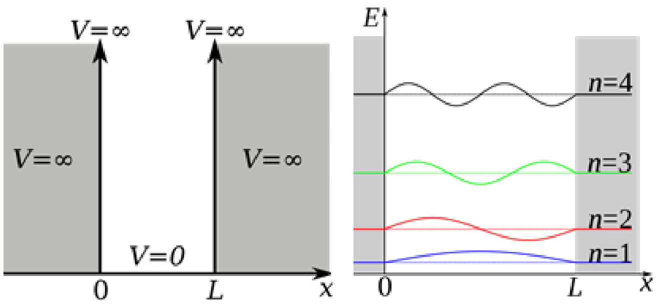
It’s essential for simulating time-based processes like chemical reactions, quantum tunneling, and light-matter interactions.

UNIT-2

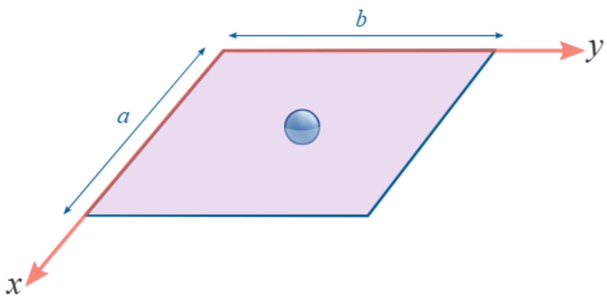
QUANTUM MODELS

Particle in a box-1D

The particle in a one-dimensional box is a fundamental quantum mechanical model. It helps explain the behavior of a particle, such as an electron, confined within fixed boundaries. The box has rigid walls, meaning the particle cannot exist outside the box, and the potential energy inside is zero. The particle is free to move within the box but is completely restricted at the boundaries. These boundaries are considered infinite potential barriers. The wave function of the particle must be zero at the walls, because the particle cannot exist there. Solving the time-independent Schrödinger equation for this system shows that only certain wave functions are allowed. These wave functions are called stationary states, and they form standing waves within the box. Each wave pattern corresponds to a specific energy level. A key result is that the energy levels are quantized, meaning the particle can only have certain discrete energy values. The lowest energy is not zero; this is called zero-point energy, a purely quantum effect. The particle can never be completely at rest inside the box. The particle's probability distribution shows where it is most likely to be found. For higher energy levels, more peaks appear in the distribution. This model explains how confinement leads to energy quantization and forms the basis for understanding quantum dots, nanostructures, and molecular orbitals.

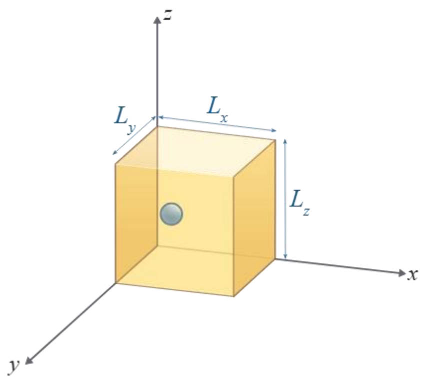


Two dimensional



The 2D particle in a box model extends the one-dimensional case to a particle confined within a rectangular or square region in two dimensions (say along x and y axes). The potential inside the box is zero, and outside it is infinite. The particle cannot escape the box, and its wave function must be zero at the boundaries. Inside the box, the particle moves freely in two directions. The Schrödinger equation can be separated into two independent one-dimensional equations -one for the x-direction and one for the y-direction. This gives rise to two quantum numbers, usually nx and ny, each corresponding to quantization along a specific axis. The total wave function is a product of the wave functions in x and y. The energy levels depend on both quantum numbers and are also quantized. Energy increases with both nx and ny, and some combinations of quantum numbers may lead to degenerate energy levels, meaning different states have the same energy. The probability density pattern for the particle changes with each pair of quantum numbers, creating nodes and antinodes (regions of zero and maximum probability). These patterns resemble standing waves in a vibrating membrane. This 2D model helps explain the behavior of particles in surfaces, thin films, quantum wells, and nanostructures. It also introduces the concept of degeneracy, which becomes important in higher dimensions and more complex systems.

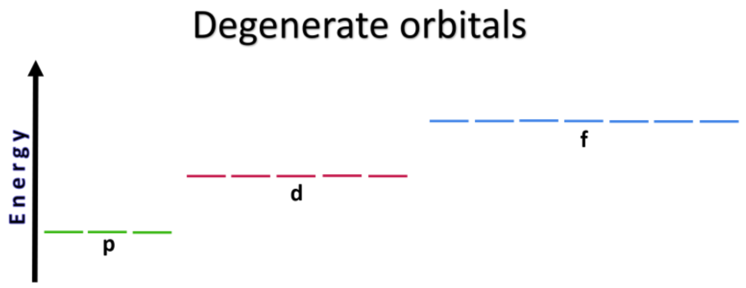
Three dimensional



The 3D particle in a box model describes a particle (like an electron) confined inside a three-dimensional rectangular box where it moves freely within but cannot escape. The potential energy inside the box is zero, and outside the box it is infinite. The particle is confined along all three axes—x, y, and z—and the wave function must be zero at the walls in all directions. The time-independent Schrödinger equation is solved separately for each dimension, resulting in a total wave function that is a product of three one-dimensional wave functions. This leads to three quantum numbers, usually denoted nx, ny, and nz. Each quantum number determines the number of half-wavelengths in that direction. The energy of the particle depends on the sum of the squares of these three quantum numbers. The energy levels are quantized, and some energy levels may be degenerate, meaning different sets of quantum numbers give the same total energy. The lowest energy is called the ground state, and higher ones are excited states. The 3D box model helps visualize how quantum confinement works in all directions, such as in quantum dots or nano-sized crystals. It also shows how complex standing wave patterns form in space, influencing the particle's probability distribution. This model is useful in solid-state physics, quantum chemistry, and nanotechnology for understanding the behavior of electrons in confined geometries.

Degeneracy

Degeneracy in quantum mechanics refers to the situation where two or more distinct quantum states have the same energy. These states differ in quantum numbers but yield equal energy values due to the symmetry of the system. Degeneracy is commonly observed in multi-dimensional systems. In the particle in a box model (2D or 3D), different combinations of quantum numbers can give the same total energy. For example, in a square box, the (2,1) and (1,2) states are degenerate. The number of such states with equal energy is called the degree of degeneracy. Degeneracy plays an important role in determining the spectral lines of atoms and molecules. In atoms, degeneracy arises from spherical symmetry and electron spin, and it's lifted (split) when external fields are applied, such as in the Zeeman effect or Stark effect. Degeneracy helps explain the distribution of electrons in energy levels, especially in Fermi-Dirac statistics. It’s also crucial for understanding selection rules, transition probabilities, and molecular orbital theory. The concept of degeneracy shows how symmetry and dimensionality influence the behavior of quantum systems.



Application to Linear Conjugated Molecular Systems

Linear conjugated molecular systems, such as butadiene or polyenes, have alternating single and double bonds. These molecules contain π-electrons that are delocalized over the entire conjugated chain. These π-electrons can be modeled using the particle in a 1D box approach. In this model, the conjugated system is treated as a 1D box of length equal to the molecular chain. The electrons are considered as free particles within this box, confined by the molecule’s length. The quantized energy levels of these electrons help explain electronic absorption spectra. When a molecule absorbs energy (like UV light), π-electrons can jump from lower to higher energy levels. The difference in energy between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) determines the wavelength of light absorbed. As the length of the conjugated system increases, the energy gap between levels decreases, causing a red shift (absorption of longer wavelengths). This explains why long conjugated systems appear colored.

This model, though simplified, helps interpret the behavior of organic dyes, retinal, and conducting polymers. It's a foundational idea in quantum chemistry and materials science.

Free Particles

A free particle in quantum mechanics is one that experiences no potential energy—it moves in space without any confinement or external forces. Unlike confined particles (like in a box), a free particle is not restricted by boundaries.The Schrödinger equation for a free particle gives solutions in the form of plane waves. These waves are not localized, meaning the particle's exact position cannot be determined—it can be anywhere with equal probability. Since the particle is not bound, its energy and momentum are continuous, not quantized. However, the particle still has wave-like properties, such as interference and diffraction. The wave function describes a delocalized state, and its square (probability density) is constant over space, which is physically unrealistic. To make it meaningful, wave packets are used—superpositions of many waves, allowing localized behavior. Free particle models are useful in scattering problems, electron transport, quantum tunneling, and metal conduction. They are the basis of understanding electrons in conductors and semiconductors. Even though idealized, the free particle concept is fundamental to quantum physics and leads to more complex models in solid-state and molecular physics.

Ring Systems

Ring systems in quantum mechanics refer to particles confined to move on a circular path, such as an electron in a planar ring molecule like benzene. These systems are modeled using the particle on a ring concept. In this model, the particle moves freely along a circular path with fixed radius, and the potential is constant along the ring. The wave function must satisfy periodic boundary conditions, meaning it must be the same at the start and end of the ring.

Solving the Schrödinger equation for this system gives quantized angular momentum and discrete energy levels. The quantum number here is angular (azimuthal), and the energy depends on its square, allowing both positive and negative values. This model explains the behavior of π-electrons in aromatic compounds, especially using Hückel's rule, which predicts aromatic stability for systems with $4n+2$π-electrons. The ring model also helps in molecular orbital theory, predicting delocalized orbitals and planar stability of molecules like benzene. It's used in spectroscopy, magnetism, and nano rings. The particle-on-a-ring model bridges basic quantum theory with real chemical systems and highlights the role of symmetry, delocalization, and quantization in ring-shaped molecules.

Harmonic Oscillator – Wave Equation and Solution

The quantum harmonic oscillator is a fundamental model that describes a particle moving in a parabolic potential well. It is used to model vibrational motion of atoms in molecules, especially near equilibrium bond lengths. The potential energy increases quadratically with displacement, similar to a spring (Hooke's law). The Schrödinger equation for this system has exact analytical solutions, making it one of the few solvable quantum problems. The wave equation includes both kinetic and potential energy terms, and solving it yields quantized energy levels. The allowed energies are evenly spaced and depend on a quantum number nnn, starting from a nonzero ground-state energy (zero-point energy). The solutions to the wave equation are given by a Gaussian function multiplied by Hermite polynomials. These wave functions describe vibrational states, each with a specific number of nodes. Unlike classical systems, the particle can never be completely at rest; it always has zero-point motion due to quantum uncertainty. The spacing between energy levels is uniform, and transitions between them obey selection rules.

The harmonic oscillator model is widely used in infrared spectroscopy, vibrational spectroscopy, phonon theory, and molecular vibrations. It gives a simplified yet powerful insight into oscillatory systems at the quantum scale.

Anharmonicity

In real molecules, atomic vibrations are not perfectly harmonic—the restoring force is not exactly proportional to displacement. This leads to anharmonicity, a deviation from the ideal harmonic oscillator model. Anharmonicity becomes significant at higher vibrational energies, where the bond may stretch far from equilibrium. In this case, the potential is no longer a perfect parabola but more like a Morse potential, which better approximates real molecular behavior. Due to anharmonicity, the spacing between energy levels is no longer uniform. The energy gap decreases with increasing quantum number, eventually leading to bond dissociation. This explains why real vibrational spectra have non-equally spaced peaks. Anharmonic effects also cause overtone transitions ($\Delta n > 1$), which are forbidden in the harmonic model but observed in real spectra. These give rise to weaker absorption bands at multiples of the fundamental frequency. Anharmonicity is essential for understanding molecular thermodynamics, heat capacity, bond breaking, and reaction dynamics. It also explains phenomena like infrared intensity changes, vibrational coupling, and anharmonic corrections in quantum chemistry.

Thus, while the harmonic oscillator is a useful approximation, anharmonicity provides a more realistic picture of molecular vibrations and energies.

Force constant and its significance

The force constant (k) is a measure of the stiffness or strength of a bond in a molecule. It originates from Hooke's law, where the restoring force is proportional to the displacement. In quantum mechanics, it appears in the potential energy term of the harmonic oscillator:

$$V(x) = \frac{1}{2}kx^2$$

A higher force constant means the bond is stiffer, requiring more energy to stretch or compress it. This directly influences the vibrational frequency of a bond—stronger bonds vibrate faster and thus have higher frequencies in the infrared (IR) region.

In spectroscopy, the force constant determines the position of absorption bands. For example, C-H bonds have higher force constants than C-C bonds, so they appear at higher frequencies in IR spectra.

The force constant also depends on bond order—triple bonds are stiffer than double or single bonds. It helps chemists assess bond strength, bond stiffness, and molecular stability.

It is also used in molecular mechanics and vibrational analysis to model how molecules deform under external forces. In quantum chemistry, calculated force constants help predict vibrational spectra and molecular structure.

Rigid Rotor – Wave Equation and Solution (20 lines)

The rigid rotor model in quantum mechanics is used to describe the rotational motion of diatomic molecules. It assumes the two atoms are connected by a rigid bond of fixed length and rotate about their center of mass. In this model, the potential energy remains constant during rotation, so the only energy considered is rotational kinetic energy. The system is described using spherical coordinates because rotation occurs in three dimensions. Solving the Schrödinger equation for a rigid rotor gives solutions known as spherical harmonics, which depend on two quantum numbers: J (rotational quantum number) and m (magnetic quantum number). The allowed energy levels are quantized and proportional to J(J+1), where J = 0, 1, 2,....

Each energy level corresponds to a specific rotational state, and transitions between these levels produce rotational spectra, typically observed in the microwave region. These transitions follow the selection rule: $\Delta J = \pm 1$.

The rigid rotor model is fundamental in molecular spectroscopy, helping scientists identify molecules and determine their rotational characteristics. Though simplified, it captures essential features of molecular rotation.

Rotational Constants and Bond Length Calculation

The rotational constant (B) is a parameter that describes how easily a molecule rotates. It depends on the moment of inertia (I) of the molecule and is inversely proportional to it. A larger molecule (or longer bond length) has a smaller rotational constant. The rotational constant is calculated from experimental microwave spectra using the formula for rotational energy levels. The spacing between lines gives B, and from B, one can calculate the bond length of a diatomic molecule. Moment of inertia depends on the reduced mass (μ) of the two atoms and the bond length (r) squared. Knowing the masses of the atoms and

B, one can solve for r. This method provides a highly accurate measurement of interatomic distances. Rotational constants are also used to determine molecular geometry, isotopic effects, and molecular identification in gas-phase spectroscopy. Isotopic substitution (e.g., H to D) changes μ, and thus B, without changing the bond length, which helps confirm molecular structure. This approach is crucial in microwave spectroscopy, astronomical molecule detection, and computational chemistry for verifying molecular models.

UNIT-3

APPLICATIONS TO HYDROGEN AND POLY ELECTRON ATOMS

Hydrogen atom and hydrogen like ions

The hydrogen atom is the simplest atom, consisting of a single electron orbiting a single proton. It serves as a fundamental model in quantum mechanics due to its exact analytical solution to the Schrödinger equation.

The Coulombic attraction between the positively charged nucleus and the negatively charged electron creates a potential energy that varies inversely with distance. Solving the Schrödinger equation for this potential gives quantized energy levels. These energy levels depend only on the principal quantum number (n). The allowed energies become more closely spaced as n increases, and the lowest energy corresponds to the ground state.

The hydrogen atom's wave function has three quantum numbers:

- n (principal) determines energy,
- l (azimuthal) determines shape of the orbital, and
- m (magnetic) determines orientation.

These wave functions explain the shapes of s, p, d orbitals, which describe the probability of finding the electron in various regions around the nucleus. Hydrogen-like ions are atoms with only one electron but a higher nuclear charge (Z), such as He^{+}, Li^{2+}, etc. Their energy levels are also quantized and scale with Z^2, meaning the electron is more tightly bound as the nuclear charge increases.

This model explains the hydrogen spectral lines, ionization energies, and forms the basis for atomic theory, quantum chemistry, and astrophysics. It is also foundational for understanding more complex atoms through approximation methods.

Hamiltonian-wav equation and solutions, radial and angular functions

The Hamiltonian operator is the total energy operator in quantum mechanics. It includes both the kinetic energy and potential energy of a system. For atoms like hydrogen, the potential energy comes from the Coulomb attraction between the nucleus and the electron.

In the case of the hydrogen atom, the Hamiltonian is used in the Schrödinger wave equation, which is solved in spherical coordinates due to the central, spherical symmetry of the Coulomb potential.

The wave function solution is separated into three parts: a radial function (depends on the distance from the nucleus), an angular function (depends on angles θ and φ), and a time-dependent part. For stationary states, the time part is ignored.

The radial function determines how the electron's probability density changes with distance from the nucleus. It depends on both n and l, and explains the size and shape of orbitals like 1s, 2s, 2p, etc.

The angular functions are given by spherical harmonics, which describe the directionality of orbitals. These depend on quantum numbers l and m. For example, p orbitals have directional lobes, while s orbitals are spherically symmetric.

The full wave function, a product of radial and angular parts, gives the orbital shapes and is crucial in understanding electron configuration, bonding, and spectroscopy.

Solving the Hamiltonian for hydrogen gives exact energy levels and orbital shapes, while for multi-electron systems, approximations are needed.

Radial Distribution Function

The radial distribution function (RDF) explains how the probability of finding an electron varies with its distance from the nucleus in an atom. In quantum mechanics, the electron in an atom is described by a wave function, which has both radial and angular components. The radial part, R(r)R(r)R(r), depends only on the distance from the nucleus. However, to calculate the actual likelihood of finding the electron at a particular radius, we must also consider the volume of the spherical shell at that radius. Therefore, the radial distribution function is given by P(r)=|R(r)|2·r2. This expression accounts for both the probability density and the increasing volume as the radius increases. The RDF tells us where the electron is most likely to be found. For hydrogen-like atoms, each orbital (1s, 2s, 2p, etc.) has a unique radial distribution. For example, the 1s orbital has a single peak close to the nucleus, while the 2s orbital has two peaks due to a radial node. The 2p orbital has one peak, but it occurs farther from the nucleus than the 1s. These distributions help in understanding atomic size, chemical bonding, and periodic trends. RDF plots typically have distance (r) on the X-axis and probability (P(r)) on the Y-axis. The area under the RDF curve gives the total probability, which is always equal to one for a normalized orbital. These concepts are important for understanding electron configurations and the behavior of atoms in molecules.

Approximation methods–variation methods

In quantum mechanics, exact solutions of the Schrödinger equation are available only for simple systems like the hydrogen atom. For more complex systems, **approximation methods** are used. One such method is the **variation method**, which provides an upper bound to the true ground state energy of a quantum system. The central idea is to assume a **trial wave function** that depends on one or more adjustable parameters. This function should satisfy the boundary conditions of the system and be physically acceptable (normalizable and continuous). The **variation integral** is then calculated as

$$E = \frac{\int \psi_{\text{trial}}^* \hat{H} \psi_{\text{trial}} \, dx}{\int \psi_{\text{trial}}^* \psi_{\text{trial}} \, dx}$$

where H is the Hamiltonian operator and ψtrial is the trial wave function. The energy E obtained is an estimate of the ground state energy. By adjusting the parameters in the trial function to minimize this energy, we get the best possible approximation.

As an example, consider a particle in a one-dimensional box of length *L*. Suppose we choose a trial wave function like ψtrial=x(L−x), which satisfies the boundary conditions (zero at the ends). We insert this function into the variation integral, perform the integration, and minimize the result if needed. This will give an approximate energy close to the actual ground state energy. Though not exact, the variation method is useful and widely applied in systems where exact solutions are not possible. It is especially valuable in molecular quantum mechanics and computational chemistry.

Perturbation method – first order applications

The perturbation method is another important approximation technique in quantum mechanics. It is used when a system’s Hamiltonian can be divided into two parts: a solvable main part and a small additional part called the perturbation. The method is based on the assumption that the extra term causes only a small change in the system's energy and wave function. Mathematically, the total Hamiltonian is written as:

H^=H^0+λH^′

where H^ $_0$ is the known Hamiltonian with known solutions, 'H^′ is the perturbation, and λ is a small parameter.

In **first-order perturbation theory**, the correction to the energy of the unperturbed state is calculated using the formula:

In first-order perturbation theory, the correction to the energy of the unperturbed state is calculated using the formula:

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

Here, $\psi n^{(0)}$ is the unperturbed wave function, and $En^{(1)}$ is the first-order correction to the energy. One simple application is the perturbed particle in a 1D box. If a small potential is added inside the box, the first-order correction to energy can be calculated using the known wave functions of the particle in a box. Another application is the Stark effect, where the energy levels of the hydrogen atom are shifted slightly in the presence of an external electric field. This shift can be computed using first-order perturbation theory. This method is especially useful in atomic and molecular systems under external fields or in slightly disturbed environments. It provides insight into how systems respond to small changes without solving the entire Schrödinger equation again.

Hatrefock self-consistent field method

The Hartree-Fock (HF) method is an important approximation technique used to solve the Schrödinger equation for multi-electron systems. Exact solutions are not possible when more than one electron is present due to complex electron-electron repulsions. In the HF method, the motion of each electron is treated as if it were moving in the average field produced by all other electrons. This is known as the mean-field approach. The total wave function of the system is constructed using a Slater determinant to maintain the antisymmetric nature of fermions. The HF method starts with an initial guess for electron orbitals. Using this guess, the effective potential is calculated and new orbitals are derived. This process is repeated iteratively until the orbitals do not change between cycles—this is called self-consistency. The result is a set of molecular orbitals and a total energy for the system. Though the method does not account for electron correlation fully, it lays the foundation for many advanced quantum chemical calculations. HF theory provides good estimates for closed-shell systems and is often the starting point for post-Hartree-Fock methods. It forms the backbone of many computational chemistry programs. The method is widely used to understand molecular structure and properties.

Hohenberg-Kohn Theorem

The Hohenberg-Kohn theorem is a fundamental result in quantum chemistry and the basis of Density Functional Theory (DFT). Proposed by Pierre Hohenberg and Walter Kohn in 1964, it states that the ground-state properties of a many-electron system are uniquely determined by its electron density. This was a significant shift from traditional wave function methods that depend on 3N variables for N electrons. In contrast, electron density is a function of just three spatial variables, making calculations simpler. The theorem has two parts: First, the ground-state density determines all observables of the system. Second, there exists a variational principle for the energy based on density. This means the correct ground-state density minimizes the total energy functional. The Hohenberg-Kohn theorem does not provide a way to construct the exact functional but proves that such a functional exists. This insight paved the way for practical DFT methods. It shows that all the complex electron interactions can, in theory, be described by a density function alone. This significantly reduces computational costs in quantum chemistry. The theorem holds true for any system with an external potential. It is particularly useful in solid-state physics, chemistry, and material science. Despite its elegance, practical use requires approximations for unknown energy functionals.

Kohn-Sham Equation

The Kohn-Sham equation is a practical implementation of the Hohenberg-Kohn theorem and forms the core of Density Functional Theory (DFT). Walter Kohn and Lu Jeu Sham introduced it in 1965 to make DFT computationally usable. It replaces the complex many-electron problem with a set of simpler equations for non-interacting electrons. These electrons are assumed to move in an effective potential that includes the external potential, electron-electron repulsion, and an exchange-correlation potential. The Kohn-Sham orbitals are mathematically similar to Hartree-Fock orbitals, but they include additional correlation effects. The electron density is obtained by summing the squared magnitudes of these orbitals. This density is then used to build the potential, and the equations are solved again—thus a self-consistent loop is formed. The Kohn-Sham method is more accurate than Hartree-Fock for many systems because it includes electron correlation through approximate functionals. The most common approximations are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). These equations have made DFT a powerful tool in computational chemistry, physics, and materials science. They are widely used to calculate molecular geometries, reaction energies, and electronic properties of solids. Despite being an approximation, it achieves a good balance between accuracy and computational cost.

Helium Atom – Electron Spin

The helium atom is the simplest multi-electron system with two electrons and one nucleus. Solving its Schrödinger equation exactly is not possible due to electron-electron repulsion. However, approximate methods help understand its behavior. One of the key quantum mechanical features in helium is **electron spin**. Each electron has an intrinsic property called spin, which can take values of +½ or –½. Due to the Pauli exclusion principle, no two electrons in the same atom can have the same set of quantum numbers. In helium, both electrons occupy the 1s orbital, but with opposite spins. This forms a spin-paired configuration and results in a singlet ground state. The electrons are indistinguishable and must be treated as fermions. The total wave function of the helium atom must be antisymmetric under exchange of electrons. This means the spatial part of the wave function is symmetric while the spin part is antisymmetric. Excited states of helium can involve spin triplets (parallel spins), leading to different energies due to reduced electron repulsion. The interplay of spin and spatial configuration determines the chemical and magnetic behavior of helium. Understanding spin in helium provides a foundation for more complex atoms and molecules. It also helps explain spectroscopy, electron configurations, and magnetic properties.

Pauli Exclusion Principle and Slater Determinant

The **Pauli exclusion principle** is a fundamental rule in quantum mechanics formulated by Wolfgang Pauli. It states that no two electrons in an atom can have the same set of four quantum numbers. This principle explains why electrons fill atomic orbitals in a specific order and is responsible for the structure of the periodic table. It applies to all fermions, which are particles with half-integer spin, like electrons. To ensure the wave function of a multi-electron system reflects this principle, it must be antisymmetric under exchange of any two electrons. To construct such antisymmetric wave functions, physicists use the **Slater determinant**. It is a mathematical formula built from single-electron wave functions (orbitals) arranged in a determinant form. When two electrons are exchanged, the determinant changes sign, satisfying the antisymmetry requirement. If two electrons occupy the same orbital, two rows in the determinant become identical, and the whole determinant becomes zero, enforcing the Pauli exclusion principle.

Slater determinants are used in the Hartree-Fock method and other quantum chemical approaches. They allow for systematic handling of electron configurations while maintaining quantum mechanical requirements. They are also used to represent both ground and excited states. Slater determinants provide a compact and accurate way to model multi-electron systems in atoms and molecules, forming a key part of computational chemistry and quantum physics.

UNIT-4

GROUP THEORY

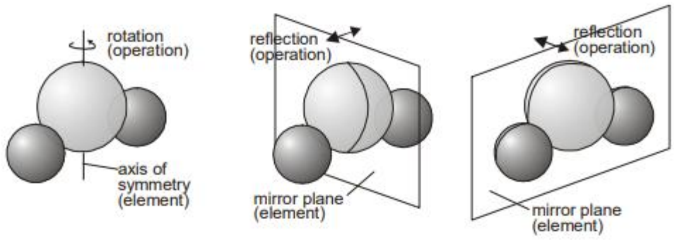
Group theory is a branch of mathematics that deals with symmetry. In chemistry, it is used to analyze the symmetrical properties of molecules and predict their physical and chemical behavior. A group is defined as a set of elements (usually symmetry operations) that follow specific mathematical rules. These operations include identity (E), rotation (Cn), reflection (σ), inversion (i), and improper rotation (Sn). A group must satisfy four conditions: closure, associativity, the existence of an identity element, and the existence of inverse elements. The symmetry operations of a molecule form a group called a point group. Group theory helps classify molecules into these point groups based on their shape and symmetry elements. Each point group has a character table that provides information about molecular vibrations, orbitals, and selection rules. Group theory simplifies the analysis of molecular vibrations and is widely used in IR and Raman spectroscopy. It also explains orbital overlaps and bonding in molecular orbital theory. The concepts of representations and matrices are used to study how molecular orbitals transform under symmetry operations. Group theory helps in predicting which electronic transitions are allowed or forbidden. It is an essential tool in understanding the structure, reactivity, and spectral properties of molecules. Overall, group theory connects the abstract idea of symmetry with practical chemical applications.

Groups and Subgroups

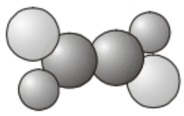
In group theory, a group is a set of elements along with a defined operation that follows four basic rules: closure, associativity, the presence of an identity element, and the existence of inverse elements. In chemistry, these elements are often symmetry operations that describe how a molecule can be transformed without changing its overall appearance. A group must have a finite or infinite set of operations that follow the group rules. For example, the set of all symmetry operations of a molecule like water forms a group called C_2v. Groups help classify molecules based on their symmetry and are essential in determining their spectroscopic and bonding properties. Within a group, a subgroup is a smaller set of operations that also satisfies the group rules. A subgroup must include the identity operation and be closed under the group operation. Every group contains at least two subgroups: the trivial subgroup (just the identity) and the group itself. Subgroups help understand how complex symmetries can be broken down into simpler components. They are also useful in constructing character tables and analyzing vibrational modes. Subgroups are key in predicting which molecular vibrations will be active in infrared or Raman spectroscopy. In essence, studying groups and subgroups allows chemists to use symmetry to interpret molecular structure and behavior efficiently.

Symmetry operations and symmetry elements

A symmetry operation is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. It will also look the same if we reflect it through either of two mirror planes, as shown in the figure below.



Each symmetry operation has a corresponding symmetry element, which is the axis, plane, line or point with respect to which the symmetry operation is carried out. The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a symmetry axis; in a reflection the points that remain unchanged make up a plane of symmetry. The symmetry elements that a molecule may possess are: 1. E - the identity. The identity operation consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule has at least this element. 2. Cn - an n-fold axis of rotation. Rotation by 360°/n leaves the molecule unchanged. The H2O molecule above has a C2 axis. Some molecules have more than one Cn axis, in which case the one with the highest value of n is called the principal axis. Note that by convention rotations are counterclockwise about the axis. 3. σ - a plane of symmetry. Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labelled σv, while one perpendicular to the axis is called a horizontal mirror plane and is labelled σh. A vertical mirror plane that bisects the angle between two C2 axes is called a dihedral mirror plane, σd. 4. i - a centre of symmetry. Inversion through the centre of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the centre of inversion and out to the same distance on the other side of the molecule. An example of a molecule with a centre of inversion is shown below.



5. Sn - an n-fold improper rotation axis (also called a rotary-reflection axis). The rotary reflection operation consists of rotating through an angle 360°/n about the axis, followed by reflecting in a plane perpendicular to the axis. Note that S1 is the same as reflection and S2 is the same as inversion. The molecule shown above has two S2 axes. The identity E and rotations Cn are symmetry operations that could actually be carried out on a molecule. For this reason they are called proper symmetry operations. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed improper symmetry operations. A note on axis definitions: Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

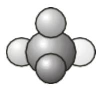
Symmetry classification of molecules – point groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called *point groups* (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labelling symmetry groups, called the *Schoenflies* and *Hermann-Mauguin* (or *International*) systems. The symmetry of individual molecules is usually described using the Schoenflies notation, and we shall be using this notation for the remainder of the course[1].

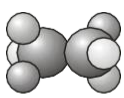
Note: Some of the point groups share their names with symmetry operations, so be careful you don't mix up the two. It is usually clear from the context which one is being referred to.
The molecular point groups are listed below.

C1 – contains only the identity (a C1 rotation is a rotation by 360° and is the same as the identity operation E) e.g. CHDFCl The molecular point groups are listed below.

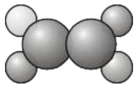
Cl - contains only the identity (a C1 rotation is a rotation by 360° and is the same as the identity operation E) e.g. CHDFCl



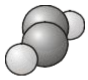
1. Ci - contains the identity E and a centre of inversion i.



2. C_S - contains the identity E and a plane of reflection σ.

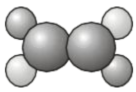


3. C_n – contains the identity and an n-fold axis of rotation.



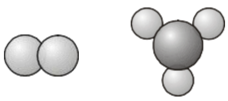
4. C_{nv} – contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.

5. C_{nh} - contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a centre of inversion).

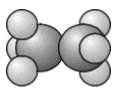


6. D_n - contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.

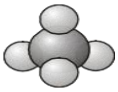
7. D_{nh} - contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.



8. D_{nd} - contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



9. S_n - contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they



have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

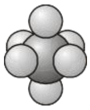
10. The following groups are the cubic groups, which contain more than one principal axis. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h). The icosahedral group also exists but is not included below.

11. T_d – contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. CH_4.

12. T - as for T_d but no planes of reflection.

13. T_h – as for T but contains a centre of inversion.

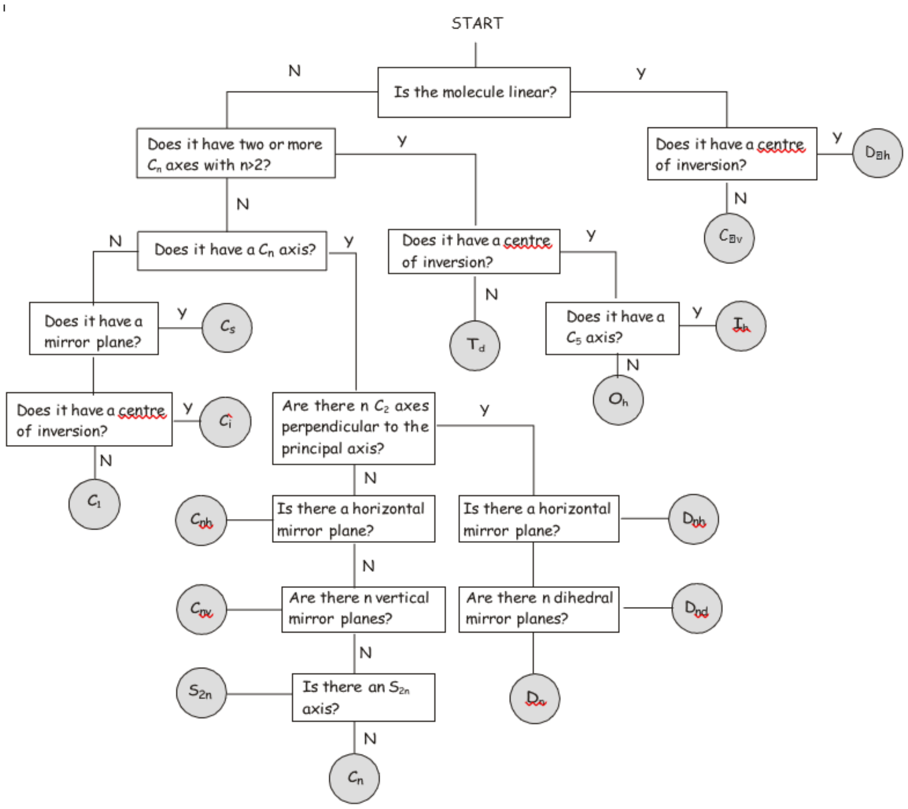
14. O_h – the group of the regular octahedron e.g. SF_6.



15. O - as for O_h but with no planes of reflection

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.



Matrix representations of groups

1. We are now ready to integrate what we have just learned about matrices with group theory. The symmetry operations in a group may be represented by a set of transformation matrices Γ(g), one for each symmetry element g. Each individual matrix is called a *representative* of the corresponding symmetry operation, and the complete set of matrices is called a *matrix representation* of the group. The matrix representatives act on some chosen *basis set* of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to *span* the chosen basis. In the examples above we were looking at the effect of some simple transformation matrices on an arbitrary vector (x,y). The basis was therefore a pair of unit vectors pointing in the x and y directions. In most of the examples we will be considering in this course, we will use sets of atomic orbitals as basis functions for matrix representations. Don't worry too much if these ideas seem a little abstract at the moment – they should become clearer in the next section when we look at some examples. Before proceeding any further, we must check that a matrix representation of a group obeys all of the rules set out in the formal mathematical definition of a group. The first thing we need to do before we can construct a matrix representation is to choose a basis. For NH3, we will select a basis (sN,s1,s2,s3) that consists of the valence s orbitals on the nitrogen and the three hydrogen atoms. We need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C3v point group, and determine the matrices that would be required

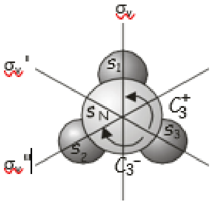
to produce the same effect. The basis set and the symmetry operations in the C3v point group are summarised in the figure below. The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.

2. The second rule is that the combination of any pair of elements must also be an element of the group (the *group property*). If we multiply together any two matrix representatives, we should get a new matrix which is a representative of another symmetry operation of the group. In fact, matrix representatives multiply together to give new representatives in exactly the same way as symmetry operations combine according to the group multiplication table. For example, in the C3v point group, we showed that the combined symmetry operation C3σv is equivalent to σv''. In a matrix representation of the group, if the matrix representatives of C3 and σv are multiplied together, the result will be the representative of σv''.

3. The third rule states that every operation must have an inverse, which is also a member of the group. The combined effect of carrying out an operation and its inverse is the same as the identity operation. It is fairly easy to show that matrix representatives satisfy this criterion. For example, the inverse of a reflection is another reflection, identical to the first. In matrix terms we would therefore expect that a reflection matrix was its own inverse, and that two identical reflection matrices multiplied together would give the identity matrix. This turns out to be true, and can be verified using any of the reflection matrices in the examples above. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first.

4. The final rule states that the rule of combination of symmetry elements in a group must be associative. This is automatically satisfied by the rules of matrix multiplication.

1.1. *Example: a matrix representation of the C3v point group (the ammonia molecule)*



The Great orthogonality theorem

The Great Orthogonality Theorem is a fundamental principle in group theory that provides mathematical relationships between the elements of group representations. It plays a crucial role in the construction and use of character tables in chemistry. This theorem applies to irreducible representations, which are the smallest building blocks of group representations. It states that the rows and columns of the matrix representations of symmetry operations are orthogonal to each other. This means the scalar product of different rows or columns equals zero, while the product of a row or column with itself gives a constant. In chemistry, instead of working with matrices, we often use the characters (traces of matrices), which also obey orthogonality relationships. These character relationships help identify how many irreducible representations exist in a group and how they behave under different symmetry operations. The theorem ensures that each irreducible representation is unique and independent of the others. It also provides a method to break down complex representations into a sum of irreducible ones. This is especially useful in vibrational spectroscopy, where the symmetry of normal modes can be analyzed. The Great Orthogonality Theorem is the foundation for predicting which vibrational transitions are IR or Raman active. It also simplifies quantum mechanical calculations by revealing symmetry-based simplifications in wave functions and integrals.

Irreducible representation and reduction formula

In group theory, a representation is a way to express the symmetry operations of a molecule as matrices. These representations can be either reducible or irreducible. A reducible representation is one that can be broken down into smaller representations, while an irreducible representation cannot be simplified further. Irreducible representations are the basic building blocks of group theory and are listed in the character table for each point group. Every symmetry operation in a group has an associated character (a number) that belongs to a particular representation. If a molecule's motion or orbital transformation gives a reducible representation, we can reduce it to a sum of irreducible representations using the reduction formula. This formula helps determine how many times each irreducible representation appears in the reducible one. It uses the characters of the reducible and irreducible representations and the order of the group. The reduction formula is very useful in analyzing vibrational modes, predicting IR and Raman activity, and understanding the symmetry of molecular orbitals. It tells us which types of vibrations (stretching, bending, etc.) belong to which symmetry species. Thus, irreducible representations and the reduction formula help interpret molecular symmetry and simplify complex quantum chemical problems using group theory.

Construction of character table for C2v, C2h, C3vand D2h point groups

Character tables are important tools in group theory that summarize the symmetry properties of molecules. Each point group has a unique character table showing how different symmetry operations affect molecular orbitals, vibrations, and electronic states. To construct a character table, we first list the symmetry operations of the point group, such as E (identity), Cn (rotation), σ (mirror plane), and i (inversion). For example, the C_2v group includes E, C_2 (rotation by 180°), σv(xz), and σv'(yz). The character table includes irreducible representations (A_1, A_2, B_1, B_2), each with its character values under these operations. The C_2h group includes E, C_2, i, and σh, with irreducible representations like Ag, Bg, Au, and Bu. In C_3v, the operations are E, C_3 (120° rotation), and three vertical planes (σv). Its character table contains irreducible representations A_1, A_2, and E. The D_2h point group has higher symmetry, including E, C_2 (x, y, z), i, and σ planes (xy, yz, zx), with eight irreducible representations such as Ag, B1g, B2u, etc. The character table also shows how atomic orbitals (s, p, d) and vibrations transform under the group's operations. These tables help predict IR and Raman activity and are essential in spectroscopy and quantum chemistry. Understanding how to construct and read character tables allows chemists to interpret molecular symmetry, vibrations, and electronic transitions more easily.

C_{2v}

	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

C_{2h}

The C_{2h} character table is, in part:

C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	−1	1	−1
A_u	1	1	−1	−1
B_u	1	−1	−1	1

C_{3v}

C_{3v}	E	$2C_3$ (z)	$3\sigma_v$	Linear functions, rotations
A_1	+1	+1	+1	z
A_2	+1	+1	-1	R_z
E	+2	-1	0	(x, y) (R_x, R_y)

D2h

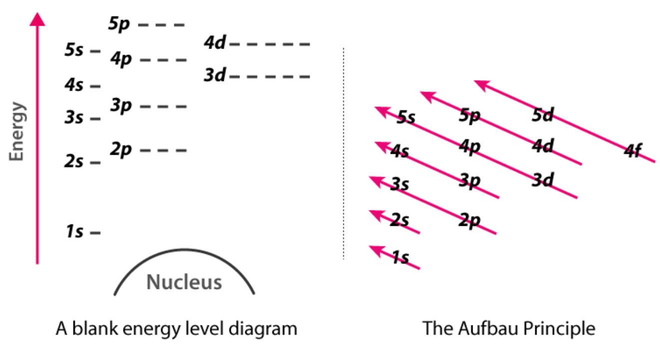
D_{2h}	E	$C_2(x)$	$C_2(y)$	$C_2(z)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
A_g	1	1	1	1	1	1	1	1
B_{1g}	1	-1	-1	1	1	1	-1	-1
B_{2g}	1	-1	1	-1	1	-1	1	-1
B_{3g}	1	1	-1	-1	1	-1	-1	1
A_u	1	1	1	1	1	-1	-1	-1
B_{1u}	1	-1	-1	1	1	-1	1	1
B_{2u}	1	-1	1	-1	1	1	-1	1
B_{3u}	1	1	-1	-1	1	1	1	-1

UNIT-5

APPLICATIONS OF QUANTUM AND GROUP THEORY

The hydrogen molecule (H_2) is often used to illustrate the two main bonding theories: Molecular Orbital (MO) Theory and Heitler–London Valence Bond (VB) Theory. In MO theory, the 1s orbitals of two hydrogen atoms combine to form two molecular orbitals: a bonding orbital (σ1s) and an antibonding orbital (σ*1s). Both electrons occupy the bonding orbital, resulting in a stable covalent bond with increased electron density between the nuclei. This explains the bond formation and gives accurate predictions of bond length and energy. In contrast, the Heitler–London VB theory describes the bond as an overlap of two atomic orbitals with one electron each, forming a covalent bond through electron pair sharing. It emphasizes electron pairing and spin and explains the bond as a result of wave function overlap and resonance between two possible electron arrangements. While MO theory gives a delocalized picture of electrons across the molecule, VB theory keeps electrons localized around atoms. Both approaches agree on the stability and properties of H_2 but offer different views. MO theory is better for explaining magnetic and spectral properties, while VB theory gives a more intuitive picture of bonding. Studying H_2 using both methods lays the foundation for understanding bonding in more complex molecules.

Energy level diagram



An energy level diagram is a visual representation that shows the relative energies of atomic or molecular orbitals and how electrons occupy them. It helps explain the electronic structure of atoms and molecules. In atoms, energy levels correspond to shells and subshells like 1s, 2s, 2p, and so on. As we move to higher levels, energy increases. In molecules, energy level diagrams show how atomic orbitals combine to form molecular orbitals. For diatomic molecules like H_2, two 1s orbitals combine to form bonding (σ1s) and antibonding (σ1s) molecular orbitals. Electrons fill these molecular orbitals based on the Aufbau principle, Pauli exclusion principle, and Hund's rule. Bonding orbitals are lower in energy, and electrons prefer to occupy them first. The energy level diagram can also show degeneracy, where orbitals have the same energy, like the 2px, 2py, and 2pz orbitals in atoms. In more complex molecules, diagrams include π and π orbitals formed from p orbital overlaps. These diagrams are essential in understanding bond order, magnetism, and electronic transitions. For example, if bonding orbitals are fully filled and antibonding orbitals are empty, the molecule is stable. Energy level diagrams are useful tools in molecular orbital theory, spectroscopy, and chemical bonding analysis.

The hydrogen molecule ion (H_2^+) is the simplest molecular system, consisting of two protons and one electron. It serves as a foundational model in quantum chemistry. To describe the electronic structure of H_2^+, approximate methods are used because exact solutions are difficult. One common method is the Linear Combination of Atomic Orbitals (LCAO) approach, where the molecular orbital is expressed as a combination of atomic orbitals from each hydrogen atom. The resulting molecular orbital can be bonding or antibonding, depending on how the wave functions combine. The bonding combination leads to increased electron density between the nuclei and stabilizes the molecule. To apply this method, the linear variation principle is used, which involves selecting a trial wave function as a linear combination of known atomic orbitals. Coefficients in this combination are adjusted to minimize the total energy using the variation method. The result is an approximate wave function and energy that closely represent the real system. The success of this method lies in choosing appropriate basis functions and minimizing the energy through the variation principle. H_2^+ helps introduce concepts like molecular orbital formation, bonding and antibonding interactions, and variational approximations. This simple ion plays a key role in understanding the quantum mechanical treatment of bonding in more complex molecules.

Electronic conjugated system: Huckel method to Ethylene butadiene

The Hückel Molecular Orbital (HMO) method is a simple quantum mechanical approach used to study the π-electron systems in conjugated organic molecules. It is particularly useful for molecules with alternating double and single bonds, where π-electrons are delocalized over the structure. The method applies to planar systems like ethylene (C_2H_4) and butadiene (C_4H_6). In ethylene, two carbon atoms are connected by a double bond, each contributing one p-orbital. These orbitals overlap to form one bonding (π) and one antibonding (π^*) molecular orbital. The two π-electrons occupy the lower-energy bonding orbital, stabilizing the molecule. In butadiene, four carbon atoms form a conjugated system with four overlapping p-orbitals. Using the Hückel method, a secular determinant is formed to solve for the energy levels of the π-system. The solution gives four π-molecular orbitals, with different energies and electron distributions. The lowest two are bonding orbitals, which get filled with four electrons. This approach provides qualitative insights into molecular stability, reactivity, and electronic transitions. Though approximate, the Hückel method successfully explains trends in UV-visible spectroscopy, resonance energy, and aromaticity. It is widely used for teaching and preliminary analysis of larger π-conjugated systems such as benzene, polyenes, and heterocycles.

Cyclopropenyl – Electronic Conjugated System

Cyclopropenyl is a three-membered ring system composed of three carbon atoms, and when it exists as the cyclopropenyl cation ($C_3H_3^+$), it becomes the smallest aromatic system. In this form, it contains 2 π-electrons delocalized over three carbon atoms, making it a conjugated cyclic system. According to Hückel's rule, a molecule is aromatic if it is planar, cyclic, fully conjugated, and has $4n + 2$ π-electrons (where n is an integer). The cyclopropenyl cation satisfies this rule with $n = 0$, giving 2 π-electrons, and is thus aromatic and unusually stable despite the ring strain. In contrast, the neutral cyclopropenyl radical or anion does not fulfill Hückel's criteria and is not aromatic. The conjugation of π-electrons in the cation form allows electron density to be spread evenly across the ring, which contributes to its stability. Its molecular orbital structure consists of one bonding orbital filled with two electrons and two degenerate empty orbitals, following the predictions of Hückel Molecular Orbital (HMO) theory. Cyclopropenyl serves as a key example in organic chemistry for understanding aromaticity in small rings, and it also plays a role in theoretical models and organometallic complexes.

Cyclobutadiene – Electronic Conjugated System

Cyclobutadiene (C_4H_4) is a four-membered cyclic compound with alternating double and single bonds, forming a conjugated π-electron system. It has 4 π-electrons, one from each carbon atom's p-orbital, delocalized over the ring. Though it appears to meet the basic criteria for aromaticity (planar, cyclic, and conjugated), it does not follow Hückel's rule, which states that aromatic compounds must have (4n + 2) π-electrons. For cyclobutadiene, n = 1 would require 6 π-electrons, but it has only 4. This makes cyclobutadiene antiaromatic, a condition that leads to instability and high reactivity. The molecule tends to distort from a square planar shape to a rectangular geometry to localize its electrons and reduce antiaromatic character. Molecular orbital (MO) analysis shows two bonding and two antibonding orbitals; filling two electrons in bonding and two in non-bonding orbitals results in an unstable electronic configuration. Cyclobutadiene is rarely found in isolation and is often studied in stabilized complexes. Its unusual behavior highlights the importance of π-electron counting and symmetry in predicting molecular stability. Cyclobutadiene is a classic example used to contrast aromatic, non-aromatic, and antiaromatic systems in organic chemistry.

Benzene – Electronic Conjugated System

Benzene (C_6H_6) is a six-membered cyclic hydrocarbon and the most well-known example of an aromatic conjugated system. Each carbon atom in benzene is sp^2 hybridized, with one unhybridized p-orbital perpendicular to the ring plane. These six p-orbitals overlap sideways to form a delocalized π-electron cloud above and below the ring. Benzene contains 6 π-electrons, which satisfy Hückel's rule (4n + 2, where n = 1), confirming its aromatic character. The π-electrons are equally distributed, giving rise to uniform bond lengths (about 1.39 Å), which are intermediate between single and double bonds. This delocalization provides benzene with extra stability known as aromatic stabilization energy. In molecular orbital theory, benzene's six π-MOs include three bonding and three antibonding orbitals; the bonding orbitals are fully occupied by the six electrons. The molecule is planar, highly symmetrical (D_6h point group), and exhibits unique chemical and physical properties like resistance to addition reactions and distinct UV-visible absorption. Benzene's structure is often represented by a hexagon with a circle inside to indicate delocalization. It plays a central role in organic chemistry and is the parent compound for numerous aromatic derivatives, pharmaceuticals, and industrial chemicals.

Applications of group theory to molecular vibrations

- ✓ Helps determine the number of vibrational modes in a molecule.
- ✓ Predicts which vibrational modes are infrared (IR) active.
- ✓ Identifies Raman active vibrational modes.
- ✓ Distinguishes between stretching and bending vibrations.
- ✓ Classifies normal modes of vibration based on symmetry species.

- ✓ Reduces complex vibrational motion into symmetry-adapted linear combinations (SALCs).
- ✓ Uses character tables to assign vibrational modes to specific irreducible representations.
- ✓ Facilitates spectral interpretation in IR and Raman spectroscopy.
- ✓ Explains degeneracy of vibrational energy levels.
- ✓ Helps in vibrational mode assignment in polyatomic molecules.
- ✓ Predicts mutual exclusion of IR and Raman activity in centrosymmetric molecules.
- ✓ Aids in constructing vibrational energy level diagrams.
- ✓ Assists in analyzing normal coordinate transformations.
- ✓ Simplifies normal mode analysis for high-symmetry molecules.
- ✓ Supports computational methods in vibrational frequency calculations.
- ✓ Provides insights into coupled vibrations and their symmetry.
- ✓ Explains the selection rules for vibrational transitions.
- ✓ Identifies inactive modes (silent in both IR and Raman).
- ✓ Used in predicting thermodynamic properties like entropy and heat capacity.
- ✓ Essential for interpreting vibrational spectra of large biomolecules and crystals.

Electronic Spectra of Ethylene

Ethylene (C_2H_4) is a simple molecule with a double bond, consisting of a π-electron system that exhibits electronic transitions upon absorption of ultraviolet (UV) light. In ethylene, each carbon is sp^2 hybridized, with unhybridized p-orbitals overlapping to form a π-bond. These π-electrons can absorb energy and be excited from the π (bonding) orbital to the *π (antibonding)** orbital, leading to a π → π* electronic transition. This transition occurs in the UV region, typically around 165 nm. The electronic spectrum of ethylene is relatively simple, as it involves only one strong absorption band due to this allowed transition. The transition is symmetry-allowed and hence has high intensity in the UV absorption spectrum. Group theory helps confirm the selection rules, showing that the π → π* transition is dipole-allowed in ethylene's D_2h symmetry. Ethylene does not show n → π* transitions because it lacks nonbonding electrons. The study of ethylene's electronic spectra provides a basic understanding of how conjugated systems absorb light, which is extended to more complex systems like dienes, polyenes, and aromatic compounds. It also plays a key role in photochemistry and spectroscopic identification of unsaturated molecules.