KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)

(Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

LECTURE PLAN

DEPARTMENT OF CHEMISTRY

Staff In charge : Dr.M.R.Ezhilarasi
Class : M.Sc Chemistry
Subject : Physical Chemistry
Subject Code : 19CHP103
Semester / Year : I/I

M.Sc. Chemistry **2019-2020**

Semester-I
19CHP103 **PHYSICAL CHEMISTRY- I** **4H 4C**
(QUANTUM CHEMISTRY AND GROUP THEORY)

Instruction Hours/week: L: 4 T: 0 P: 0 Marks: Internal: 40 External: 60 Total:100
External Semester Exam: 3 Hrs

Course Objectives

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.

Course Outcomes

Students have learned and understood

1. The differences between classical and quantum mechanics. The limitations of classical mechanics.
2. the connection of quantum mechanical operators to observables
3. probabilities, amplitudes, averages, expectation values, and observables
4. how molecular phenomena can be related to model problems
5. the fundamentals of group theory

6. the connection between common approximation methods and standard chemical frameworks (Born-Oppenheimer approximation, molecular orbitals, for example)
7. Identified the point groups of molecules and apply the concept of group theory to predict the spectroscopic properties.

UNIT I – Failure of classical mechanics and Operators

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.

KAHE

UNIT II – Schrodinger equation

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 – Approximation 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.

UNITIV – Symmetry elements and Matrices

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 – Group theory

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

1. Prasad, R. K. (2004). 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. (2002). Quantum Chemistry (IV Edition). New Delhi: Tata McGraw – Hill Publishing Company Ltd.
4. House, J. E. (2003). Fundamental of Quantum Chemistry (II Edition). New Delhi: Academic Press.
5. Levine, I. N. (2004). Quantum Chemistry (V Edition). New Delhi: Pearson Education Pvt. Ltd.
6. Raman, K.V. (2002). Group Theory and its Applications to Chemistry. New Delhi: Tata McGraw Publishing Company.
7. Puri, B. R., Sharma, L. R., &Pathania, M. S. (2013). Principles of Physical Chemistry (46th Edition). Jalandar: Vishal Publishing Co.
8. Veera Reddy, K. (2009). Symmetry and Spectroscopy of Molecules. New Delhi: New Age International Pvt. Ltd.
9. Atkins, P., & De Paula, J. (2014). Atkins Physical Chemistry (X Edition). Oxford: Oxford University Press.

KAHE

KAHE

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)

(Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

LECTURE PLAN

DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr.M.R.EZHILARASI
CLASS: I M.Sc
SUBJECT NAME: PHYSICAL CHEMISTRY-I (Quantum Chemistry & group theory)
SUB.CODE:19CHP103
SEMESTER: I -Odd semester (CHEMISTRY)
YEAR : 2019-2020

S.No	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
	UNIT-I		
1	1	Failure of Classical mechanics and Operators: Introduction, Block body radiation and quantum theory	T1:3-7
2	1	Photoelectric effect	T1:7-11
3	1	The time dependent and time independent Schrodinger equations	T1:25-27
4	1	Requirements of the acceptable wave functions	T1:27-29
5	1	Operators: Algebra of operators, sum and products of operator, commutator-linear operator	T1:34-37
6	1	Eigen function and eigen values	T1:37-40
7	1	Basic postulates of quantum mechanics	T1:40-48
8	1	Momentum operator, Hamiltonian operator, angular momentum operator	T1:42-43

9	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit 1=9		
	UNIT-II		
1	1	Schrodinger equation: Introduction, Free Particle system	T1:65-67
2	1	Particle in a one dimensional box, Quantization of energy	T1:67-70
3	1	Normalization of the wave function, Orthogonality of the particle in a one dimensional box wave functions	T1:70-79
4	1	Particle in a ring	T1:119-122
5	1	Particle in a three dimensional box, separation of variables	T1:122-123,123-124
6	1	Schrodinger equation for one dimensional harmonic oscillator-Classical mechanical treatment	T1:104-106
7	1	Quantum mechanical treatment	T1:106-113
8	1	A comparison of classical and Quantum mechanical treatment	T1:113
9	1	Solving the Schrodinger equation for a rigid rotor: (rigid rotor model of diatomic molecules)	T1:136-138
10	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit II=10		
	UNIT-III		
1	1	Approximation methods: Schrodinger equation for H-atom	T1:142-144
2	1	Separation of variables	T1:146-153

3	1	Radial distribution functions, orbitals and orbital shapes	T1:153-159
4	1	Method of perturbation-The perturbation theory	T1:192-194
5	1	First order perturbation	T1:194-202
6	1	Second order perturbation	T1:202-204
7	1	Variation method to system such as anhormonic oscillator	T1:185-192
8	1	Multielectronic atoms (He-atom)	T1:223-239
9	1	Slater determinants	T1:239-240
10	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit III=10		
	UNIT-IV		
1	1	Symmetry elements and symmetry operations	T2:1-7
2	1	Commutative, non commutative and inverse operations	
3	1	Group and their basic properties: Definition of groups and their types	T2:7-12
4	1	Symmetry classification in to point groups-Scheonflies symbol	T2:14-29
5	1	Matrices- Definitions and their types	T2:43-47
6	1	Multiplication,commutative and noncommutative determination of inverse of a matrix	T2:47-51
7	1	Character table for C_2V point groups	T2:83-84
8	1	Character table for C_3V point groups	T2:62-63
9	1	Recapitulation and discussion of	

		important questions	
	Total No of Hours Planned For Unit IV=9		
		UNIT-V	
1	1	Definition of reducible and irreducible representations	T2:52-57
2	1	Irreducible representations as orthogonal vectors	T2:61
3	1	Direct product rule	T2:100-102
4	1	The great orthogonalty theorm	T2:59-60
5	1	Group theory and vibrational spectroscopy-vibrational modes as basis for group representation	T2:79-86
6	1	Symmetry selection rule for IR and Raman	T2:104-105
7	1	Mutual exclusion principle classification of vibrational modes	T2:105-106
8	1	Recapitulation and discussion of important questions	
9	1	Discussion of previous ESE question papers	
10	1	Discussion of previous ESE question papers	
	Total No of Hours Planned for unit V=10		
Total Planned Hours	**48**		

References:

TEXT BOOKS

T1: Prasad .R.K (2008) Quantum Chemistry(III Edition) New Delhi.New Age International Publishers pvt.Ltd.

T2: Raman.K.V (2002) Group Theory and its Applications to chemistry.New delhi. Tata Mc graw Publishing company.

LECTURE NOTES

Unit-1 Failure of classical mechanics and Operators:

SYLLABUS

UNIT I – Failure of classical mechanics and Operators

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.

Failure of classical mechanics and the success of quantum theory in explaining block body radiation:

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.

Figure 1.1.1 Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature. In fact, we can be much more precise: **a body emits radiation at a given temperature and frequency *exactly* as well as it absorbs the same radiation**. This was proved by Gustav Kirchhoff: the essential point is that if we suppose a particular body can absorb better than it emits, then in a room full of objects all at the same temperature, it will absorb radiation from the other bodies better than it radiates energy back to them. This means it will get hotter, and the rest of the room will grow colder, contradicting the second law of thermodynamics. However, a metal glows when it’s heated up enough (Figure 1.1.11.1.1): why is that? As the temperature is raised, the lattice of atoms vibrates more and more, these vibrations scatter and accelerate the electrons. Even glass glows at high enough temperatures, as the electrons are loosened and vibrate.

Any body at any temperature above absolute zero will radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter*.

So how do we construct a perfect absorber in the laboratory? OK, nothing’s perfect, but in 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we’re going to find (Figure 1.1.21.1.2).

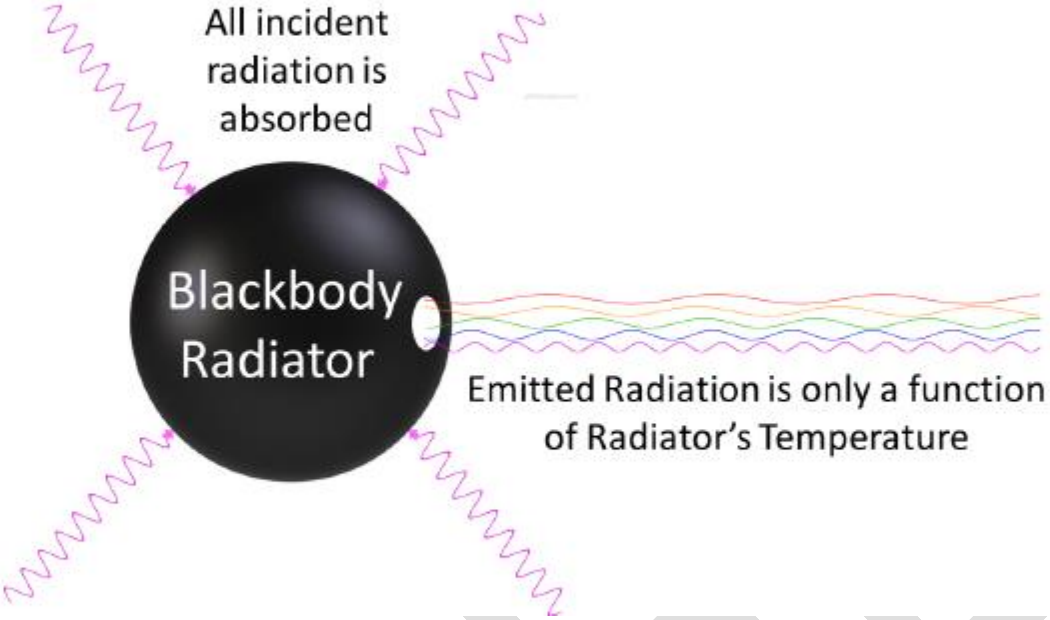


Figure 1.1.21.1.2: Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation.

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution of blackbody radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven, and began to measure the radiation coming out. The beam coming out of the hole was passed through a diffraction grating, which sent the different wavelengths/frequencies in different directions, all towards a screen. A detector was moved up and down along the screen to find how much radiant energy was being emitted in each frequency range. They found a radiation intensity/frequency curve close to the distributions in Figure 1.1.31.1.3.

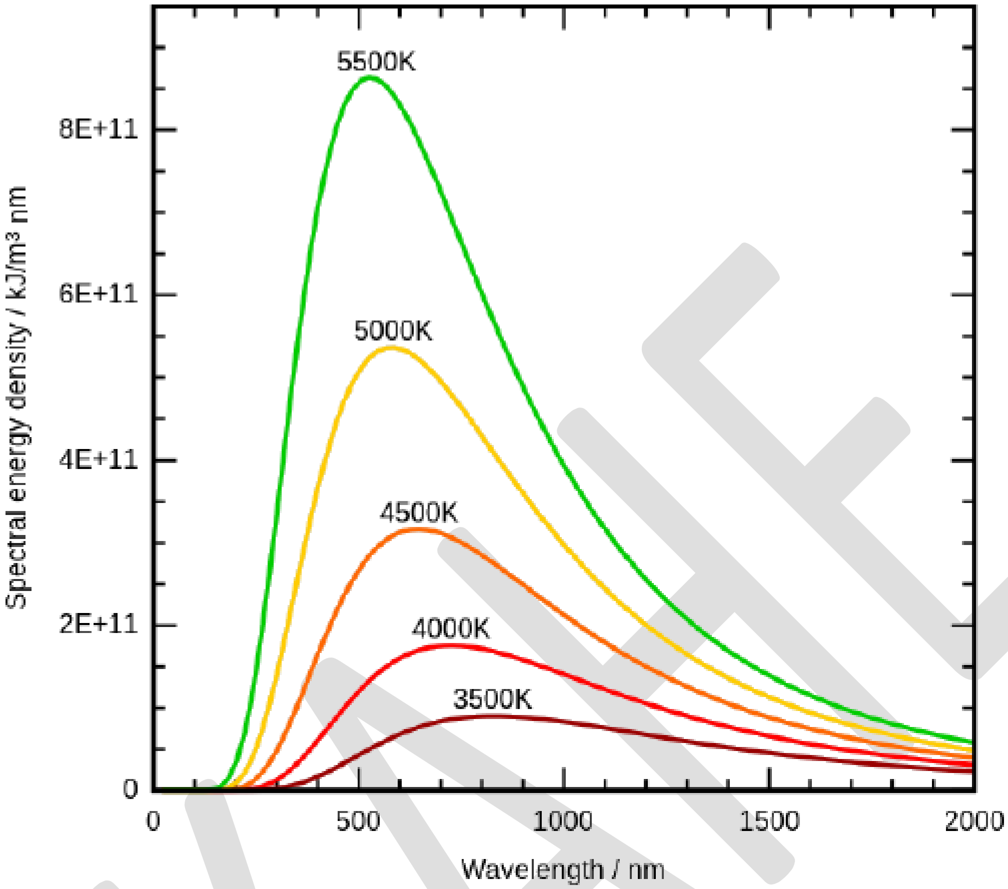


Figure 1.1.31.1.3: Graphic representation of spectral distribution of blackbody radiation at different temperatures. Image used with permission (CC-SA-BY 3.0; 4C). The Stefan-Boltmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature.

By measuring the blackbody emission curves at different temperatures (Figure 1.1.31.1.3), they were also able to construct two important phenomenological Laws (i.e., formulated from experimental observations, not from basic principles of nature): **Stefan-Boltmann's Law** and **Wien's Displacement Law**.

1.2. The photoelectric effect

The *photoelectric effect*, the emission of electrons by a metal when light falls on it, was discovered by Hertz in 1887. Experiments showed the following characteristics of this effect. When light falls on a metal surface in a vacuum, the emission of electrons depends upon the frequency of the incident light. There is a minimum frequency of light which is required for the emission of electrons from a metal. The value of this threshold frequency varies from metal to metal. The emission of electrons as well as the energy of the emitted electrons, *photoelectrons*, does not depend upon the intensity of the light source. However, if electrons are emitted, then the magnitude of their current is proportional to the intensity of the incident light. Finally, the energy of the photoelectrons varies linearly with the frequency of the light.

The classical theory of electromagnetic radiation can explain some of these characteristics but not all of them. Credit for solving this problem goes to Einstein who, in 1905, refined and extended the ideas Planck used to explain the black body radiation spectrum and assumed that 'light consists of quanta of energy, called photons'. In fact, Planck had introduced the concept of material resonators possessing quanta of energy $nh\nu$, where n is an integer, while Einstein assumed that each quantum of light possesses the energy $h\nu$. The absorption of a single photon by an electron increases the energy of the electron by $h\nu$. Part of this energy is used to remove the electron from the metal. This is called the *work function*. The remaining part of the energy imparted to the electron increases its velocity and consequently its kinetic energy. Thus if $h\nu$, the energy of a photon incident on a metal is greater than the energy E required to separate the electron from the metal, and v is the velocity of the emitted electron, then the following relation must hold:

All the characteristics of this effect are easily explained by the concept that light consists of photons. The above formula shows that if the energy of the incident photon is less than the work function, the electrons cannot be separated from the surface of the metal and therefore will not be emitted. For a particular metal, the work function E being constant, the relationship between the energy of the incident photon and the kinetic energy of the emitted electron is linear. It is also clear that a more intense source of light will cause photons to be emitted at a greater speed and this will produce a stronger electron current. Thus Einstein was able to provide a completely satisfactory picture of the photoelectric effect by using the concept of the quantum nature of light.

In fact, the dual nature of light is brilliantly reflected by the very assumption Einstein made about the energy of a photon. The frequency is determined by the wave nature of light and is used to define the energy of the particles constituting the light.

It is interesting to note that, in 1921, Einstein was awarded the Nobel Prize in physics 'for his services to Theoretical Physics and especially for his discovery of the law of the photoelectric effect' and *not*for propounding special relativity in 1905 and general relativity in 1915. His extraordinarily remarkable work on relativity changed the complexion of the entire field of physics and ensured him a seat among the immortals of the subject, but surprisingly this magnificent contribution to the pool of knowledge was never considered *specifically* for that enviable prize!

KAHE

KAHE

The Schrödinger Equation

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

The Time-Independent Schrödinger Equation

Here we follow the treatment of McQuarrie [1], Section 3-1. We start with the one-dimensional classical wave equation,

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \tag{10}$$

By introducing the separation of variables

$$u(x,t) = \psi(x) f(t) \tag{11}$$

we obtain

$$f(t)\frac{d^2\psi(x)}{dx^2} = \frac{1}{v^2}\psi(x)\frac{d^2 f(t)}{dt^2} \tag{12}$$

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

$$\frac{d^2\psi(x)}{dx^2} = \frac{-\omega^2}{v^2}\psi(x) \tag{13}$$

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

$$E = \frac{p^2}{2m} + V(x) \tag{14}$$

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

$$p = \{2m[E - V(x)]\}^{1/2} \tag{15}$$

Now we can use the de Broglie formula (4) to get an expression for the wavelength

$$\lambda = \frac{h}{p} = \frac{h}{\{2m[E - V(x)]\}^{1/2}} \tag{16}$$

The term ω^2/v^2 in equation (13) can be rewritten in terms of λ if we recall that $\omega = 2\pi\nu$ and $\nu\lambda = v$.

KAHE

$$\frac{\omega^2}{v^2} = \frac{4\pi^2\nu^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m[E - V(x)]}{\hbar^2} \tag{17}$$

When this result is substituted into equation (13) we obtain the famous *time-independent Schrödinger equation*

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 \tag{18}$$

which is almost always written in the form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{19}$$

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{20}$$

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

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

The Time-Dependent Schrödinger Equation

We are now ready to consider the time-dependent Schrödinger equation. Although we were able to derive the single-particle time-independent Schrödinger equation starting from the classical wave equation and the de Broglie relation, the time-dependent Schrödinger equation cannot be derived using elementary methods and is generally given as a postulate of quantum mechanics. It is possible to show that the time-dependent equation is at least *reasonable* if not derivable, but the arguments are rather involved (cf. Merzbacher [2], Section 3.2; Levine [3], Section 1.4).

The single-particle three-dimensional time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t) \tag{21}$$

where V is assumed to be a real function and represents the potential energy of the system (a complex function V will act as a source or sink for probability, as shown in Merzbacher [2], problem 4.1). *Wave Mechanics* is the branch of quantum mechanics with equation (21) as its dynamical law. Note that equation (21) does not yet account for spin or relativistic effects.

Of course the time-dependent equation can be used to derive the time-independent equation. If we write the wavefunction as a product of spatial and temporal terms, $\psi(\mathbf{r},t) = \psi(\mathbf{r})f(t)$, then equation (21) becomes

$$\psi(\mathbf{r})i\hbar\frac{df(t)}{dt} = f(t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) \tag{22}$$

or

$$\frac{i\hbar}{f(t)}\frac{df}{dt} = \frac{1}{\psi(\mathbf{r})}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) \tag{23}$$

Since the left-hand side is a function of t only and the right hand side is a function of $\mathbf{r}$ only, the two sides must equal a constant. If we tentatively designate this constant E (since the right-hand side clearly must have the dimensions of energy), then we extract two ordinary differential equations, namely

$$\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{iE}{\hbar} \tag{24}$$

and

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{25}$$

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

$$f(t) = e^{-iEt/\hbar} \tag{26}$$

The Hamiltonian in equation (25) is a Hermitian operator, and the eigenvalues of a Hermitian operator must be real, so E is real. This means that the solutions $f(t)$ are purely oscillatory, since $f(t)$ never changes in magnitude (recall Euler's formula $e^{\pm i\theta} = cos\theta \pm i\ sin\theta$). Thus if

$$\psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar} \tag{27}$$

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

$$|\psi(\mathbf{r},t)|^2 = \psi^*(\mathbf{r},t)\psi(\mathbf{r},t) = e^{iEt/\hbar}\psi^*(\mathbf{r})e^{-iEt/\hbar}\psi(\mathbf{r}) = \psi^*(\mathbf{r})\psi(\mathbf{r}) \tag{28}$$

Secondly, the expectation value for any time-independent operator is also time-independent, if $\psi(\mathbf{r},t)$ satisfies equation (27). By the same reasoning applied above,

$$< A >= \int \psi^*(\mathbf{r},t)\hat{A}\psi(\mathbf{r},t) = \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r}) \tag{29}$$

For these reasons, wave functions of the form (27) are called *stationary states*. The state $\psi(\mathbf{r},t)$ is ``stationary," but the particle it describes is not!

Of course equation (27) represents a particular solution to equation (21). The general solution to equation (21) will be a linear combination of these particular solutions, i.e.

$$\psi(\mathbf{r},t) = \sum_i c_i e^{-iE_i t/\hbar} \psi_i(\mathbf{r}) \qquad (30)$$

Operators

Levine [3] defines an *operator* as ``a rule that transforms a given function into another function" (p. 33). The differentation operator d/dx is an example--it transforms a differentiable function $f(x)$ into another function $f'(x)$. Other examples include integration, the square root, and so forth. Numbers can also be considered as operators (they multiply a function). McQuarrie [1] gives an even more general definition for an operator: ``An *operator* is a symbol that tells you to do something with whatever follows the symbol" (p. 79). Perhaps this definition is more appropriate if we want to refer to the $\hat{C}_3$ operator acting on NH_3, for example.

Operators and Quantum Mechanics

In quantum mechanics, physical observables (e.g., energy, momentum, position, etc.) are represented mathematically by operators. For instance, the operator corresponding to energy is the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{1}{m_i} \nabla_i^2 + V \qquad (31)$$

where i is an index over all the particles of the system. We have already encountered the single-particle Hamiltonian in equation (25). The average value of an observable A represented by an operator $\hat{A}$ for a quantum molecular state $\psi(\mathbf{r})$ is given by the ``expectation value" formula

$$< A >= \int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d\mathbf{r} \qquad (32)$$

Basic Properties of Operators

Most of the properties of operators are obvious, but they are summarized below for completeness.

- The **sum** and **difference** of two operators $\hat{A}$ and $\hat{B}$ are given by

$$(\hat{A}+\hat{B})f = \hat{A}f+\hat{B}f \tag{33}$$

$$(\hat{A}-\hat{B})f = \hat{A}f-\hat{B}f \tag{34}$$

-
- The **product** of two operators is defined by

$$\hat{A}\hat{B}f \equiv \hat{A}[\hat{B}f] \tag{35}$$

-
- Two operators are **equal** if

$$\hat{A}f=\hat{B}f \tag{36}$$

-
- for all functions f .
- The **identity operator** $\hat{1}$ does nothing (or multiplies by 1)

KAHE

$$\hat{1} f = f \tag{37}$$

-
- A common mathematical trick is to write this operator as a sum over a complete set of states (more on this later).

$$\sum_i |i\rangle\langle i| f = f \tag{38}$$

-
- The **associative law** holds for operators

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{39}$$

-
- The **commutative law** does *not* generally hold for operators. In general, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. It is convenient to define the quantity

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{40}$$

- which is called the **commutator** of $\hat{A}$ and $\hat{B}$. Note that the order matters, so that $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$. If $\hat{A}$ and $\hat{B}$ happen to commute, then $[\hat{A}, \hat{B}] = 0$.
- The **n-th power** of an operator $\hat{A}^n$ is defined as n successive applications of the operator, e.g.

KAHE

$$\hat{A}^2 f = \hat{A}\hat{A}f \qquad (41)$$

- The **exponential** of an operator $e^{\hat{A}}$ is defined via the power series

$$e^{\hat{A}} = \hat{1} + \hat{A} + \frac{\hat{A}^2}{2!} + \frac{\hat{A}^3}{3!} + \cdots \qquad (42)$$

Linear Operators

Almost all operators encountered in quantum mechanics are *linear operators*. A linear operator is an operator which satisfies the following two conditions:

$$\hat{A}(f+g) = \hat{A}f + \hat{A}g \qquad (43)$$

$$\hat{A}(cf) = c\hat{A}f \qquad (44)$$

where c is a constant and f and g are functions. As an example, consider the operators d/dx and $()^2$. We can see that d/dx is a linear operator because

$$(d/dx)[f(x)+g(x)] = (d/dx)f(x) + (d/dx)g(x) \qquad (45)$$

$$(d/dx)[cf(x)] = c\,(d/dx)f(x) \qquad (46)$$

However, $()^2$ is not a linear operator because

$$(f(x)+g(x))^2 \neq (f(x))^2+(g(x))^2 \tag{47}$$

The only other category of operators relevant to quantum mechanics is the set of *antilinear* operators, for which

$$\hat{A}(\lambda f+\mu g)=\lambda^*\hat{A}f+\mu^*\hat{A}g \tag{48}$$

Time-reversal operators are antilinear (cf. Merzbacher [2], section 16-11).

Eigenfunctions and Eigenvalues

An *eigenfunction* of an operator $\hat{A}$ is a function f such that the application of $\hat{A}$ on f gives f again, times a constant.

$$\hat{A}f=kf \tag{49}$$

where k is a constant called the *eigenvalue*. It is easy to show that if $\hat{A}$ is a linear operator with an eigenfunction g, then any multiple of g is also an eigenfunction of $\hat{A}$.

When a system is in an *eigenstate* of observable A (i.e., when the wavefunction is an eigenfunction of the operator $\hat{A}$) then the expectation value of A is the eigenvalue of the wavefunction. Thus if

$$\hat{A}\psi(\mathbf{r}) = a\psi(\mathbf{r}) \tag{50}$$

then

$$\begin{aligned} < A > &= \frac{\int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})d\mathbf{r}}{} \\ &= \frac{\int \psi^*(\mathbf{r})a\psi(\mathbf{r})d\mathbf{r}}{} \\ &= \frac{a\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}}{} \\ &= a \end{aligned} \tag{51}$$

assuming that the wavefunction is normalized to 1, as is generally the case. In the event that $\psi(\mathbf{r})$ is not or cannot be normalized (free particle, etc.) then we may use the formula

$$< A >= \frac{\int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r})}{d}\mathbf{r}\int \psi^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} \tag{52}$$

KAHE

What if the wavefunction is a combination of eigenstates? Let us assume that we have a wavefunction which is a linear combination of two eigenstates of $\hat{A}$ with eigenvalues $\underline{a}$ and $\underline{b}$.

$$\psi = c_a\psi_a + c_b\psi_b \tag{53}$$

where $\hat{A}\psi_a = a\psi_a$ and $\hat{A}\psi_b = b\psi_b$. Then what is the expectation value of A?

$$\begin{aligned} \langle A \rangle &= \underline{\int \psi^* \hat{A}\psi} \\ &= \underline{\int [c_a\psi_a + c_b\psi_b]^* \hat{A} [c_a\psi_a + c_b\psi_b]} \\ &= \underline{\int [c_a\psi_a + c_b\psi_b]^* [ac_a\psi_a + bc_b\psi_b]} \\ &= \underline{a|c_a|^2 \int \psi_a^*\psi_a + bc_a^*c_b \int \psi_a^*\psi_b + ac_b^*c_a \int \psi_b^*\psi_a + b|c_b|^2 \int \psi_b^*\psi_b} \\ &= a|c_a|^2 + b|c_b|^2 \end{aligned} \tag{54}$$

assuming that ψ_a and ψ_b are orthonormal (shortly we will show that eigenvectors of Hermitian operators are orthogonal). Thus the average value of A is a weighted average of eigenvalues, with the weights being the squares of the coefficients of the eigenvectors in the overall wavefunction.

KAHE

Hermitian Operators

As mentioned previously, the expectation value of an operator $\hat{A}$ is given by

$$< A >= \int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d\mathbf{r} \qquad (55)$$

and all physical observables are represented by such expectation values. Obviously, the value of a physical observable such as energy or density must be real, so we require $< A >$ to be real. This means that we must have $< A >=< A >^*$, or

$$\int \psi^*(\mathbf{r}) \hat{A} \psi(\mathbf{r}) d\mathbf{r} = \int (\hat{A}\psi(\mathbf{r}))^* \psi(\mathbf{r}) d\mathbf{r} \qquad (56)$$

Operators $\hat{A}$ which satisfy this condition are called *Hermitian*. One can also show that for a Hermitian operator,

$$\int \psi_1^*(\mathbf{r}) \hat{A} \psi_2(\mathbf{r}) d\mathbf{r} = \int (\hat{A}\psi_1(\mathbf{r}))^* \psi_2(\mathbf{r}) d\mathbf{r} \qquad (57)$$

for any two states ψ_1 and ψ_2.

An important property of Hermitian operators is that their eigenvalues are real. We can see this as follows: if we have an eigenfunction of $\hat{A}$ with eigenvalue a, i.e. $\hat{A}\psi_a = a\psi_a$, then for a Hermitian operator $\hat{A}$

$$\int \psi_a^* \hat{A} \psi_a = \int \psi_a (\hat{A}\psi_a)^* \qquad (58)$$

$$a \int \psi_a^* \psi_a = a^* \int \psi_a \psi_a^*$$

$$(a - a^*) \int |\psi_a|^2 = 0$$

Since $|\psi_a|^2$ is never negative, we must have either $a = a^*$ or $\psi_a = 0$. Since $\psi_a = 0$ is not an acceptable wavefunction, $a = a^*$, so a is real.

Another important property of Hermitian operators is that their eigenvectors are orthogonal (or can be chosen to be so). Suppose that ψ_a and ψ_b are eigenfunctions of $\hat{A}$ with eigenvalues a and b, with $a \neq b$. If $\hat{A}$ is Hermitian then

$$\int \psi_a^* \hat{A} \psi_b = \int \psi_b (\hat{A}\psi_a)^* \qquad (59)$$

$$b \int \psi_a^* \psi_b = a^* \int \psi_b \psi_a^*$$

$$(b - a) \int \psi_a^* \psi_b = 0$$

since $a = a^*$ as shown above. Because we assumed $b \neq a$, we must have $\int \psi_a^* \psi_b = 0$, i.e. ψ_a and ψ_b are orthogonal. Thus we have shown that eigenfunctions of a Hermitian operator with different eigenvalues are orthogonal. In the case of degeneracy (more than one eigenfunction with the same eigenvalue), we can *choose* the eigenfunctions to be orthogonal. We can easily show this for the case of two eigenfunctions of $\hat{A}$ with the same eigenvalue. Suppose we have

$$\hat{A}\psi_j = j\psi_j \qquad (60)$$

$$\hat{A}\psi_k = j\psi_k$$

We now want to take linear combinations of ψ_j and ψ_k to form two new eigenfunctions $\psi_{j'}$ and $\psi_{k'}$, where $\psi_{j'} = \psi_j$ and $\psi_{k'} = \psi_k + c\psi_j$. Now we want $\psi_{j'}$ and $\psi_{k'}$ to be orthogonal, so

$$\int \psi_{j'}^* \psi_{k'} = 0 \qquad (61)$$

$$\int \psi_j^* (\psi_k + c\psi_j) = 0$$

$$\int \psi_j^* \psi_k + c \int \psi_j^* \psi_j = 0$$

Thus we merely need to choose

$$c = -\frac{\int \psi_j^* \psi_k}{\int \psi_j^* \psi_j} \qquad (62)$$

and we obtain orthogonal eigenfunctions. This Schmidt-orthogonalization procedure can be extended to the case of n-fold degeneracy, so we have shown that for a Hermitian operator, the eigenvectors can be made orthogonal.

Unitary Operators

A linear operator whose inverse is its adjoint is called *unitary*. These operators can be thought of as generalizations of complex numbers whose absolue value is 1.

$$U^{-1} = U^\dagger \qquad (63)$$

$$UU^\dagger = U^\dagger U = I$$

A unitary operator preserves the ``lengths'' and ``angles'' between vectors, and it can be considered as a type of rotation operator in abstract vector space. Like Hermitian operators, the eigenvectors of a unitary matrix are orthogonal. However, its eigenvalues are not necessarily real.

Commutators in Quantum Mechanics

The *commutator*, defined in section 3.1.2, is very important in quantum mechanics. Since a definite value of observable A can be assigned to a system only if the system is in an eigenstate of $\hat{A}$, then we can simultaneously assign definite values to two observables A and B only if the system is in an eigenstate of both $\hat{A}$ and $\hat{B}$. Suppose the system has a value of A_i for observable A and B_j for observable B. The we require

$$\hat{A}\psi_{A_i,B_j} = A_i\psi_{A_i,B_j} \quad (64)$$

$$\hat{B}\psi_{A_i,B_j} = B_j\psi_{A_i,B_j}$$

If we multiply the first equation by $\hat{B}$ and the second by $\hat{A}$ then we obtain

$$\hat{B}\hat{A}\psi_{A_i,B_j} = \hat{B}A_i\psi_{A_i,B_j} \quad (65)$$

$$\hat{A}\hat{B}\psi_{A_i,B_j} = \hat{A}B_j\psi_{A_i,B_j}$$

and, using the fact that ψ_{A_i,B_j} is an eigenfunction of $\hat{A}$ and $\hat{B}$, this becomes

$$\hat{B}\hat{A}\psi_{A_i,B_j} = A_iB_j\psi_{A_i,B_j} \quad (66)$$

$$\hat{A}\hat{B}\psi_{A_i,B_j} = B_jA_i\psi_{A_i,B_j}$$

so that if we subtract the first equation from the second, we obtain

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi_{A_i,B_j} = 0 \quad (67)$$

For this to hold for general eigenfunctions, we must have $\hat{A}\hat{B} = \hat{B}\hat{A}$, or $[\hat{A}, \hat{B}] = 0$. That is, for two physical quantities to be simultaneously observable, their operator representations must commute.

Section 8.8 of Merzbacher [2] contains some useful rules for evaluating commutators. They are summarized below.

$$[\hat{A}, \hat{B}] + [\hat{B}, \hat{A}] = 0 \tag{68}$$

$$[\hat{A}, \hat{A}] = 0 \tag{69}$$

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \tag{70}$$

$$[\hat{A} + \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] + [\hat{B}, \hat{C}] \tag{71}$$

KAHE

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \tag{72}$$

$$[\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}] \tag{73}$$

$$[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{C}, [\hat{A}, \hat{B}]] + [\hat{B}, [\hat{C}, \hat{A}]] = 0 \tag{74}$$

If $\hat{A}$ and $\hat{B}$ are two operators which commute with their commutator, then

$$[\hat{A}, \hat{B}^n] = n\hat{B}^{n-1}[\hat{A}, \hat{B}] \tag{75}$$

$$[\hat{A}^n, \hat{B}] = n\hat{A}^{n-1}[\hat{A}, \hat{B}] \tag{76}$$

We also have the identity (useful for coupled-cluster theory)

KAHE

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{B} + [\hat{A},\hat{B}] + \frac{1}{2!}[\hat{A},[\hat{A},\hat{B}]] + \frac{1}{3!}[\hat{A},[\hat{A},[\hat{A},\hat{B}]]] + \cdots \quad (77)$$

Finally, if $[\hat{A},\hat{B}] = i\hat{C}$ then the uncertainties in A and B, defined as $\Delta A^2 =< A^2 > - < A >^2$, obey the relation[1]

$$(\Delta A)(\Delta B) \geq \frac{1}{2}| < C > | \quad (78)$$

This is the famous Heisenberg uncertainty principle. It is easy to derive the well-known relation

$$(\Delta x)(\Delta p_x) \geq \frac{\hbar}{2} \quad (79)$$

from this generalized rule.

Postulates of Quantum Mechanics

1. The state of a quantum mechanical system is completely specified by the wavefunction $\Psi(\mathbf{r},t)$.
2. To every observable in classical mechanics, there corresponds a linear, Hermitian operator in quantum mechanics. For example, in coordinate space, the momentum

KAHE

operator $\hat{P}_x$ corresponding to momentum p_x in the x direction for a single particle is $-i\hbar\frac{\partial}{\partial x}$.

3. In any measurement of the observable associated with operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a which satisfy $\hat{A}\Psi = a\Psi$. Although measurements must always yield an eigenvalue, the state does not originally have to be in an eigenstate of $\hat{A}$. An arbitrary state can be expanded in the complete set of eigenvectors of $\hat{A}$ ($\hat{A}\psi_i = a_i\psi_i$) as $\Psi = \sum_i c_i\psi_i$, where the sum can run to infinity in principle. The probability of observing eigenvalue a_i is given by $c_i^* c_i$.
4. The average value of the observable corresponding to operator $\hat{A}$ is given by

$$\langle A \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi d\tau}. \quad (3)$$

5. The wavefunction evolves in time according to the time-dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar\frac{\partial \Psi}{\partial t} \quad (4)$$

The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin must be included in this set of coordinates. The Pauli exclusion principle is a direct result of this antisymmetry principle.

References:

1. Prasad, R. K. (2004). Quantum Chemistry (II Edition). New Delhi: New Age International Publishers Pvt. Ltd.

2. Chandra, A. K. (2002). Quantum Chemistry (IV Edition). New Delhi: Tata McGraw – Hill Publishing Company Ltd.
3. Puri, B. R., Sharma, L. R., &Pathania, M. S. (2013). Principles of Physical Chemistry (46th Edition). Jalandar: Vishal Publishing Co.

POSSIBLE QUESTIONS:

Part-A (20 x 1= 20 marks) Online Examinations

(Each Question Carry 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 characteristi

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. 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

6. Black body radiation has a characteristic continuous spectrum of radiation which depends upon

KAHE

a. **Body's temperature** b. Nature of the body

c. Colour of the body d. Density of the body

7.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

8. 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

9.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

a. **Atomic orbital**
b. Molecular orbital
c. Nodal plane
d.Median lobes

10. This involves with the knowledge of probability
a. Quantum mechanics b. Classical mechanics
c. Newtonian mechanics d. Fluid mechanics

11. The knowledge of quantum mechanics usually involves a knowledge of
a. **Probability** b. certainties
c. uncertainties d. possibility

12. Classical mechanics and quantum mechanics tend to give the same results when systems are in highly excited quantum states. This is
a. Correspondence principle b. Bohrs theory
c. Rutherford theory d. Paulis exclusion principle

13. Classical mechanics and quantum mechanics tend to give the same results when systems are in
a. Normal states **b. Highly excited quantum states**
c. Excited to low levels d. When there is no excitation

KAHE

KAHE

14. In quantum mechanics the state of a system is defined by

a. Wave function	b. P,V, T
c. Gaseous laws	d. Law of mass action

15. Simuntaneous specification of position and momentum is impossible for a microscopic particle. This is

a. Stefan Boltzmann law	b. Weins displacement law
c. Planck's law	**d. Heisenberg uncertainty principle**

16. According to Newtons second law of motion

a. F = ma	b.V = ma
c. F = mv	d. F = Pv

17. Which one of the following is correct in respect of an electron and a proton having same de-Broglie wavelength of 2 Å

a. Both have same KE	b. The KE of proton is more than that of electron
c. Both have same velocity	**d. Both have same momentum**

18. The time independent Schrodinger's equation of a system represents the conservation of the

a. total binding energy of the system	b. total potential energy of the system
c. total kinetic energy of the system	**d. total energy of the system**

19. According to Schrodinger, a particle is equivalent to a

a. wave packet	b. single wave
c. light wave	d. magnetic wave

20. Matter waves are

a. longititudinal	b. electromagnetic
c. always travel with the speed of light	**d. show diffraction**

PART- B Questions (Each question carries Six mark)

1. Explain the different postulates of Quantum mechanics.
2. Explain Heisenberg's uncertainty principle .How it is experimentally verified?
3. Write a note on quantum mechanical operators?
4. Set up Schrodinger wave equation for the rigid rotor of diatomic molecules.
5. Set up Schrödinger wave equation for one dimensional box and solve the equation for its energy and wave equation.

6. Give an explanatory note on time dependent Schrodinger equation.
7. S.T.Wein's and Rayleigh Jeans law are the limiting cases of Plank's expression.
8. Give a detailed account on Hamiltonian operators.
9. Explain black body radiation and Photoelectric effect.
10. Write the postulates of Quantum mechanics.
11. Describe the linear operator with an suitable example.

PART- C (Question carries ten mark)

1. Schrodinger equation to a particle in one dimensional box.
2. What are the Postulates of quantum mechanics?
3. Give an detail account of Black body radiation?

KAHE

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
I M.SC CHEMISTRY (2019-2021 BATCH)
SUBJECT: PHYSICAL CHEMISTRY-I (QUANTUM CHEMISTRY AND GROUP THEORY)
SUBJECT CODE: 19CHP103
MULTIPLE CHOICE QUESTIONS(EACH QUESTION CARRY ONE MARK)
UNIT-1

S. NO	Question	Option A	Option B	Option C	Option D	Answer
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	uncertanities	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

KAHE

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	Simuntaneous 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 Newtons 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 Å	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

KAHE

11	According to Schrodinger, a particle is equivalent to a	wave packet	single wave	light wave	magnetic wave	wave packet
12	Matter waves are	longititudinal	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	$\lambda= h/\sqrt{mqV}$	$\lambda= hm/\sqrt{qV}$	$\lambda= h/\sqrt{2mqV}$	$\lambda= h/mqV$	$\lambda= h/\sqrt{2mqV}$
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 Kroneckers 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	Additing 1	Dividing by 2	Multiplying by 2	Multiplying by zero

KAHE

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	Hamilitonian	hermitian	Laplacian	Eigen function	Hamilitonian
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	Substracting 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	Commute	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 consequtive operations with two or more operators on a function is called as	Multiplication operator	Addition operator	Substracting 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

KAHE

KAHE

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 (Psi) will be	contineous	Discontinuous first derivative	Do not vanish at infinity	Multiple valued	contineous

KAHE

42	One of the properties of the acceptable wavefunction (Psi)	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 (Psi)	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

KAHE

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 light	Laser action	Continuous spectrum
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

KAHE

LECTURE NOTES

Unit-2 Schrodinger equation:

SYLLABUS

UNIT II – Schrodinger equation

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.

Particle in a One-Dimensional Box

A particle in a 1-dimensional box is a fundamental quantum mechanical approximation describing the translational motion of a single particle confined inside an infinitely deep well from which it *cannot* escape.

Introduction

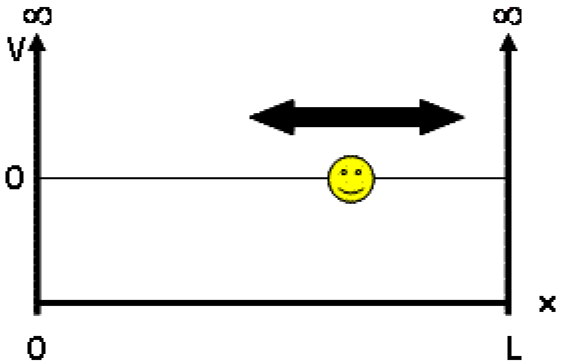
The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E and $\psi\psi$ that the particle can possess. E represents allowed energy values and $\psi(x)\psi(x)$ is a wavefunction, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

To solve the problem for a particle in a 1-dimensional box, we must follow our **Big, Big recipe for Quantum Mechanics:**

1. Define the Potential Energy, *V*
2. Solve the Schrödinger Equation

3. Define the wavefunction
4. Define the allowed energies

Step 1: Define the Potential Energy *V*



A particle in a 1D infinite potential well of dimension LL.

The potential energy is *0 inside the box* (V=0 for 0<x<L) and *goes to infinity at the walls of the box* (V=∞ for x<0 or x>L). We assume the walls have infinite potential energy to ensure that the particle has zero probability of being at the walls or outside the box. Doing so significantly simplifies our later mathematical calculations as we employ these **boundary conditions** when solving the Schrödinger Equation.

Step 2: Solve the Schrödinger Equation

The time-independent Schrödinger equation for a particle of mass *m* moving in one direction with energy *E* is

$$-\frac{\hbar 2}{2m}+\frac{d^2\Psi(x)}{dx2}+V(x)\Psi(x)=E\Psi(x) \qquad (1)$$

with

- $\hbar\hbar$ is the reduced Planck Constant where $\hbar$=h2π$\hbar$=h2π
- m is the mass of the particle
- ψ(x)ψ(x) is the stationary time-independent wavefunction
- V(x) is the potential energy as a function of position
- EE is the energy, a real number

This equation can be modified for a particle of mass *m* free to move parallel to the x-axis with zero potential energy (V = 0 everywhere) resulting in the quantum mechanical description of free motion in one dimension:

$$-\ \frac{\hbar 2}{2m}+\frac{d^2\Psi(\mathrm{x})}{dx2}=E\Psi(x) \qquad (2)$$

This equation has been well studied and gives a general solution of:

$$\Psi(x)=A\sin(kx)+\ Bcos\,(kx) \qquad (3)$$

where A, B, and k are constants.

Step 3: Define the wavefunction

The solution to the Schrödinger equation we found above is the general solution for a 1-dimensional system. We now need to apply our **boundary conditions** to find the solution to our particular system. According to our boundary conditions, the probability of finding the particle at x=0 or x=L is zero. When x=0x=0, sin(0)=0sin(0)=0, and cos(0)=1cos(0)=1; therefore, *B must equal 0* to fulfill this boundary condition giving:

$$\Psi(x)=A\sin(kx) \qquad (4)$$

We can now solve for our constants (A and k) systematically to define the wavefunction.

Solving for k
Differentiate the wavefunction with respect to x:

$$\frac{d\Psi}{dx}=kA\cos(kx) \qquad (5)$$

$$\frac{d2\Psi}{dx}=-k2A\cos(kx) \qquad (6)$$

Since ψ(x)=Asin(kx), then

$$d_2\psi/dx_2=-k_2\psi \qquad (7)$$

If we then solve for k by comparing with the Schrödinger equation above, we find:

$$k=(8\pi_2mE/h_2)_{1/2} \qquad (8)$$

Now we plug k into our wavefunction:

$$\psi=A\sin(8\pi_2mE/h_2)_{1/2}x(9)$$

Solving for A
To determine A, we have to apply the boundary conditions again. Recall that the *probability of finding a particle at x = 0 or x = L is zero.*

When x=Lx=L:

$$0=A\sin(8\pi_2mE/h_2)_{1/2}L$$

This is only true when

$$(8\pi^2 mE/h^2)^{1/2}L=n\pi$$

where n = 1,2,3…

Plugging this back in gives us:

$$\psi=A\ \sin\ n\pi/L\ x$$

To determine AA, recall that the total probability of finding the particle inside the box is 1, meaning there is no probability of it being outside the box. When we find the probability and set it equal to 1, we are *normalizing* the wavefunction.

$$\int_0^L \psi^2 dx = 1$$

For our system, the normalization looks like:

$$A^2 \int_L^0 \sin^2 (n\pi/L)\ x dx=1 \quad (10)$$

Using the solution for this integral from an integral table, we find our normalization constant, A:

$$A=\sqrt{2}/L \qquad (11)$$

Which results in the normalized wavefunction for a particle in a 1-dimensional box:

$$\psi=\sqrt{2}/L\ \sin n\pi/Lx \qquad (12)$$

Step 4: Determine the Allowed Energies

Solving for E results in the allowed energies for a particle in a box:

$$E_n=n^2h^2/8mL^2 \qquad (13)$$

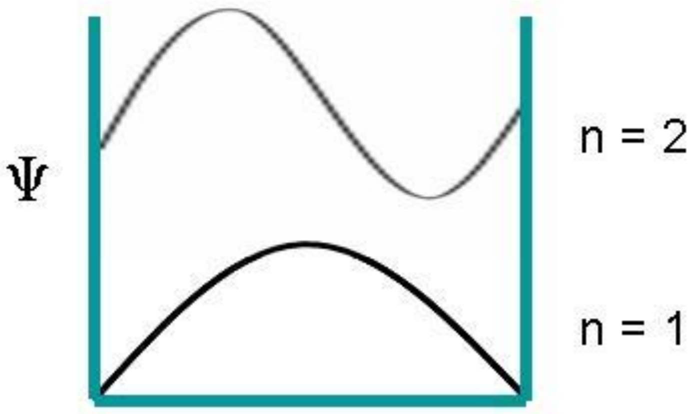
This is an important result that tells us:

1. The energy of a particle is quantized and
2. The lowest possible energy of a particle is **NOT** zero. This is called the **zero-point energy** and means the particle can never be at rest because it always has some kinetic energy.

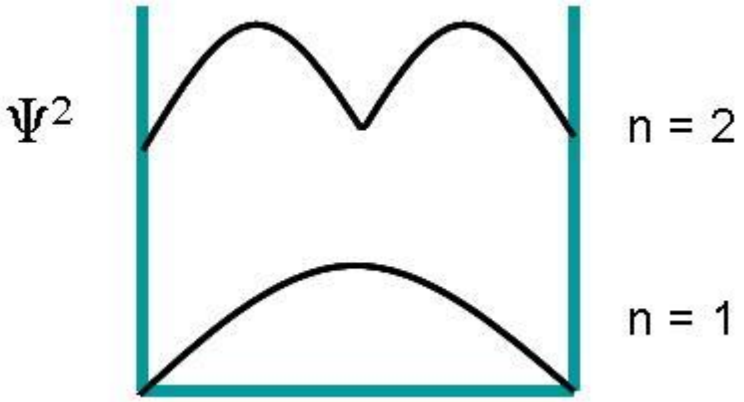
This is also consistent with the Heisenberg Uncertainty Principle: if the particle had zero energy, we would know where it was in both space and time.

What does all this mean?

The wavefunction for a particle in a box at the $n=1n=1$ and $n=2n=2$ energy levels look like this:



The probability of finding a particle a certain spot in the box is determined by squaring ψψ. The probability distribution for a particle in a box at the n=1n=1 and n=2n=2 energy levels looks like this:



Notice that the number of **nodes** (places where the particle has zero probability of being located) increases with increasing energy n. Also note that as the energy of the particle becomes greater, the quantum mechanical model breaks down as the energy levels get closer together and overlap, forming a continuum. This continuum means the particle is free and can have any energy value. At such high energies, the classical mechanical model is applied as the particle behaves more like a continuous wave. Therefore, the particle in a box problem is an example of Wave-Particle Duality.

IMPORTANT FACTS TO LEARN FROM THE PARTICLE IN THE BOX

- The energy of a particle is quantized. This means it can only take on discreet energy values.
- The lowest possible energy for a particle is **NOT** zero (even at 0 K). This means the particle *always* has some kinetic energy.
- The square of the wavefunction is related to the probability of finding the particle in a specific position for a given energy level.

- The probability changes with increasing energy of the particle and depends on the position in the box you are attempting to define the energy for
- In classical physics, the probability of finding the particle is independent of the energy and the same at all points in the box

Particle in a three-dimensional box

- Generalization of the results for a two-dimensional square box to a three-dimensional cubic box is straightforward. Since we live in a three-dimensional world, this generalization is an important one, and we need to be able to think about energy levels and wave functions in three dimensions. The potential energy $V(x,y,z)$ for the cubic box is defined to be 0 if $x \in [0,L]$, $y \in [0,L]$ and $z \in [0,L]$ and infinite otherwise. This means that the wave function $\psi(x,y,z)$ must satisfy six boundary conditions $\psi(0,y,z)=0$, $\psi(x,0,z)=0$, $\psi(x,y,0)=0$, $\psi(L,y,z)=0$, $\psi(x,L,z)=0$ and $\psi(x,y,L)=0$.

  We first note that the classical energy is the sum of three terms

$$\frac{p_x^2}{2m}+\frac{p_y^2}{2m}+\frac{p_z^2}{2m}=E$$

where p_x, p_y and p_z are the three components of the particle's momentum vector $\mathbf{p}$. Thus, we can write the energy as

$$E=\varepsilon_x+\varepsilon_y+\varepsilon_z$$

corresponding to the kinetic energy in the x, y and z directions. Because the energy is a simple sum of energies for the x, y and z directions, the wave function will be a product of wave function forms for the one-dimensional box, and in order to satisfy the first three of the boundary conditions, we can take the $\sin$ functions:

$$\psi(x,y,z) = A\sin\left(\sqrt{\frac{2m\varepsilon_x}{\hbar^2}}x\right)\sin\left(\sqrt{\frac{2m\varepsilon_y}{\hbar^2}}y\right)\sin\left(\sqrt{\frac{2m\varepsilon_z}{\hbar^2}}z\right)$$

As in the two-dimensional case, applying second three boundary conditions yields the allowed values of ε_x, ε_y and ε_z, which now require three integers n_x, n_y and n_z:

$$\varepsilon_{n_x} = \frac{\hbar^2\pi^2}{2mL^2}n_x^2 \qquad \varepsilon_{n_y} = \frac{\hbar^2\pi^2}{2mL^2}n_y^2 \qquad \varepsilon_{n_z} = \frac{\hbar^2\pi^2}{2mL^2}n_z^2$$

so that the allowed values of the total energy are

$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

and the wave functions become

$$\psi_{n_x n_y n_z}(x,y,z) = A\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)$$

The constant A is determined from the normalization condition

$$\int_0^L \int_0^L \int_0^L |\psi_{n_x n_y n_z}(x,y,z)|^2 dx\,dy\,dz = 1$$

$$A^2 \int_0^L \sin^2\left(\frac{n_x \pi x}{L}\right) dx \int_0^L \sin^2\left(\frac{n_y \pi y}{L}\right) dy \int_0^L \sin^2\left(\frac{n_z \pi z}{L}\right) dz = 1$$

$$A^2 \frac{L}{2} \cdot \frac{L}{2} \cdot \frac{L}{2} = 1$$

$$A = \left(\frac{2}{L}\right)^{3/2}$$

Thus, the wave functions are

$$\psi_{n_x n_y n_z}(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

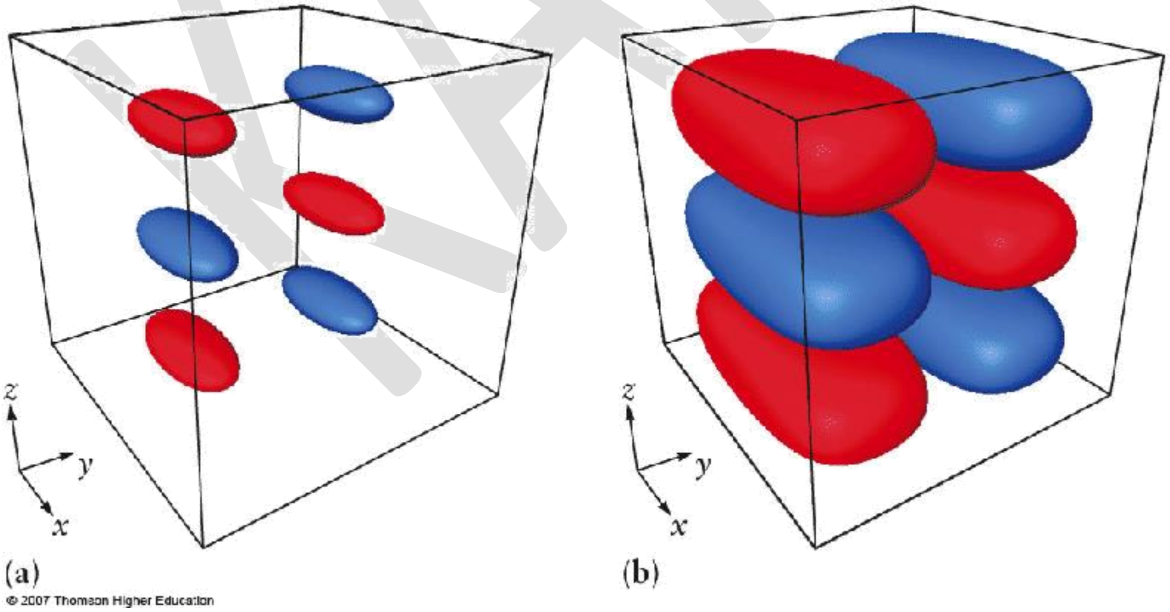
As with the two-dimensional box, the three integers n_x, n_y and n_z are restricted to the natural numbers 1,2,3,.... Thus, the lowest energy or ground-state energy is

$$E_{111} = \frac{3\hbar^2\pi^2}{2mL^2}$$

KAHE

Visualizing the wave functions is tricky because of their high dimensionality. The most common method of visualizing functions of three variables is the use of an *isosurface*. An isosurface of a function $f(x,y,z)$ is the complete set of points x, y, and z for which $f(x,y,z)=C$, where C is a chosen constant. Hence the name *isosurface* - the value of the function $f(x,y,z)$ is the same at all points on the surface.

For wave functions, where the sign can be positive or negative, it is useful to base the value of C not on the wave function value but rather on the probability density $p_{n_x n_y n_z}(x,y,z) = |\psi_{n_x n_y n_z}(x,y,z)|^2$. The figure below shows two isosurfaces of the wave function $\psi_{123}(x,y,z)$. The first occurs at a probability density value of 0.64 and the other occurs at 0.04. These value then imply that the wave function can have a fixed positive or negative value along the surface. In one case, $\psi_{123}(x,y,z) = \pm 0.8$, while in the other, $\psi_{123}(x,y,z) = \pm 0.2$.



(a) (b)

© 2007 Thomson Higher Education

Figure: Isosurfaces of $\psi_{123}(x,y,z)$ at probability density values of 0.64 and 0.04. Red is positive and blue is negative.

As in the two-dimensional case, the fact that the wave function $\psi_{n_x n_y n_z}(x,y,z)$ is a product

$$\psi_{n_x n_y n_z}(x,y,z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$$

means that the probabilities can be calculated from products of one-dimensional integrals. The probability that a measurement of a particle's position yields a value $x \in [a,b]$, $y \in [c,d]$ and $z \in [f,g]$ is

$$P(x \in [a,b] \text{ and } y \in [c,d] \text{ and } z \in [f,g]) = \int_a^b dx \int_c^d dy \int_f^g dz\, |\psi_{n_x n_y n_z}(x,y,z)|^2$$

$$= \left[\int_a^b \psi_{n_x}^2(x)dx\right]\left[\int_c^d \psi_{n_y}^2(y)dy\right]\left[\int_f^g \psi_{n_z}^2(z)dz\right]$$

The Quantum Harmonic Oscillator

Rachel Dudik

Harmonic motion is one of the most important examples of motion in all of physics. Any vibration with a restoring force equal to Hooke's law is generally caused by a simple harmonic oscillator. The potential for the harmonic ocillator is the natural solution every potential with small oscillations at the minimum. Almost all potentials in nature have small oscillations at the minimum, including many systems studied in quantum mechanics. Here, harmonic motion plays a fundamental role as a stepping stone in more rigorous applications.

The Harmonic Oscillator is characterized by the its Schrӧdinger Equation. This equation is presented in section 1.1 of this manual. The harmonic oscillator has only discrete energy states as is true of theone-dimensional particle in a box problem. The equation for these states is derived in section 1.2. An exact solution to the harmonic oscillator problem is not only possible, but also relatively easy to compute given the proper tools. It is one of the first applications of quantum mechanics taught at an introductory quantum level. Systems with nearly unsolvable equations are often broken down into smaller systems. The solution to this simple system can then be used on them. A firm understanding of the principles governing the harmonic oscillator is prerequisite to any substantial study of quantum mechanics.

1 Solution of the Schrodinger Equation

1.1 The Schrodinger Equation for the Harmonic Oscillator

The classical potential for a harmonic oscillator is derivable from Hooke’s law. It is conventionally written:

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

Where ω is the natural frequency, k is the spring constant, and m is the mass of the body.

$$\omega = \sqrt{\frac{k}{m}} \tag{2}$$

For convenience in this calculation, the potential for the harmonic oscillator is written

$$V(x) = \frac{1}{2}m\omega^2x^2 \tag{3}$$

Placing this potential in the one dimensional, time-independent Schrӧdinger equation, it yeilds:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}+\frac{1}{2}m\omega^2x^2\Psi=E\Psi \tag{4}$$

which equals:

$$\frac{d^2\Psi}{dx^2}+\left(\frac{2mE}{\hbar^2}-\frac{m^2\omega^2}{\hbar^2}x^2\right)\Psi=0 \tag{5}$$

The Equation for the Quantum Harmonic Oscillator is a second order differential equation that can be solved using a power series. In following section, 2.2, the power series method is used to derive the wave function and the eigenenergies for the quantum harmonic oscillator.

1.2 The Power Series Method

The first step in the power series method is to perform a change of variables by introducing the dimensionless variable, y[1]:

$$y=\sqrt{\frac{m\omega}{\hbar}}x \tag{6}$$

Substituting this new variable into Equation (5) above yeilds:

$$\frac{d^2\Psi(y)}{dy^2}+(\frac{2E}{\hbar\omega}-y^2)\Psi(y)=0 \tag{7}$$

For very large values of y, the term $\frac{2E}{\hbar\omega}$ is negligible in comparison to the y^2 term. With this fact we can guess that $\Psi(y)$ will be as $e^{◆\frac{y^2}{2}}$. The general solution to the differential equation is:

$$\Psi(y) = u(y)e^{\frac{-y^2}{2}} \tag{8}$$

We must now calculate the derivatives of Ψ that will be substitued into the Schrӧdinger equation.

$$\frac{d\Psi(y)}{dy} = \frac{du(y)}{dy}e^{\frac{-y^2}{2}} + (-y)u(y)e^{\frac{-y^2}{2}} \tag{9}$$

and

$$\frac{d^2\Psi(y)}{dy^2} = \frac{d^2u(y)}{dy^2}e^{\frac{-y^2}{2}} + (-y)\frac{du(y)}{dy}e^{\frac{-y^2}{2}} + (-y)\frac{du(y)}{dy}e^{\frac{-y^2}{2}} + u(y)(-1+y^2)e^{\frac{-y^2}{2}} \tag{10}$$

Putting the values from (8) and (10) in equation (7):

$$\frac{d^2u(y)}{dy^2}e^{\frac{-y^2}{2}} + (-2y)\frac{du(y)}{dy}e^{\frac{-y^2}{2}} + u(y)(-1+y^2)e^{\frac{-y^2}{2}} + (\frac{2E}{\hbar\omega} - y^2)u(y)e^{\frac{-y^2}{2}} = 0 \tag{11}$$

Canceling terms:

$$\frac{d^2u(y)}{dy^2}e^{\frac{-y^2}{2}} - (2y)\frac{du(y)}{dy}e^{\frac{-y^2}{2}} - u(y)e^{\frac{-y^2}{2}} + \frac{2E}{\hbar\omega}u(y)e^{\frac{-y^2}{2}} = 0 \tag{12}$$

And dividing through by $e^{\frac{-y^2}{2}}$, we obtain:

$$\frac{d^2u(y)}{dy^2} - (2y)\frac{du(y)}{dy} + (\frac{2E}{\hbar\omega} - 1)u(y) = 0 \tag{13}$$

The next step is to solve the second order differential equation (13) above for u(y) so that we can find an exact solution for $\Psi(y)$. We begin by using a power series of y as the general solution to equation (13). u(y) then takes the form below:

$$u(y) = \sum_{0}^{\infty} \alpha_n y^n \tag{14}$$

In order to substitute this solution into equation (13) we have to solve the first and second derivatives of u(y):

$$\frac{du(y)}{dy} = \sum_{0}^{\infty} (n) \alpha_n y^{n-1} \tag{15}$$

and,

$$\frac{d^2u(y)}{dy^2} = \sum_{0}^{\infty} (n-1)(n) \alpha_n y^{n-2} \tag{16}$$

Replacing the u(y) values in equation (13) we have:

$$\sum_{0}^{\infty} (n-1)(n) \alpha_n y^{n-2} - \sum_{0}^{\infty} (2y)(n) \alpha_n y^{n-1} + (\frac{2E}{\hbar\omega} - 1) \sum_{0}^{\infty} \alpha_n y^n = 0 \tag{17}$$

Simplifying the second term:

$$\sum_{0}^{\infty} (n-1)(n) \alpha_n y^{n-2} + (\frac{2E}{\hbar\omega} - 1 - 2n) \sum_{0}^{\infty} \alpha_n y^n = 0 \tag{18}$$

Replacing n with (n+2) in the first term. See section 4, *Math Moves and Helpful Hints*, for a discussion of this substitution.

$$\sum_{0}^{\infty} ((n+2)-1)(n+2) \alpha_{(n+2)} y^{(n+2)-2} + (\frac{2E}{\hbar\omega} - 1 - 2n)) \sum_{0}^{\infty} \alpha_n y^n = 0 \tag{19}$$

and simplifying we have:

$$\sum_{0}^{\infty}[(n+2)(n+1))\alpha_{(n+2)}+(\frac{2E}{\hbar\omega}-1-2n)\alpha_n)]y^{2n}=0 \tag{20}$$

we can then solve for α_{n+2}, because the coefficient for each power of y must equal zero (RHS of equation (20)):

$$\alpha_{n+2}=\frac{2n+1-\frac{2E}{\hbar\omega}}{(n+2)(n+1)}\alpha_n \tag{21}$$

Equation (21) is a series representation of all the expansion coefficients in terms of α_0 for the power series solution to equation (13). For large values of y, n is also very large. The ratio of α_{n+1} and α_n (from formula (21) for the coefficients of the power series expansion above) is very close to $\frac{2}{n}$. Here we have a problem, because in the limit, $\frac{2}{n}$ grows faster than the exponential term in $\Psi(y)$. The series must terminate in order for our solution to have any physical meaning. The best way to terminate the series is to equate the numerator in equation (21) with zero. We then have:

$$2n+1-\frac{2E}{\hbar\omega}=0 \tag{22}$$

We can now solve for energy, E:

$$E=\frac{\hbar\omega}{2}(2n+1)=(n+\frac{1}{2})\hbar\omega \tag{23}$$

We have found an infinite number of energies for each energy level, n. The formula for the wave function is incomplete, however, because the power series solution is incomplete. The individual eigenstates of the Hamiltonian must be made orthogonal. Hermite polynomials need be incorporated into the final solution in order to do this. What results is a function of the form:

$$\Psi(x)=\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\frac{1}{\sqrt{2^n n!}}\left[\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}x\right]e^{\frac{-m\omega}{2\hbar}x^2} \tag{24}$$

KAHE

The following is a table for the first 5 eigenenergies and eigenstates for the harmonic oscillator:[2]:

n = 0	$E = \frac{\hbar\omega}{2}$		$\Psi = \alpha_0 e^{\frac{-y^2}{2}}$
n = 1	$E = \frac{3\hbar\omega}{2}$		$\Psi = \alpha_0(2y)e^{\frac{-y^2}{2}}$
n = 2	$E = \frac{5\hbar\omega}{2}$		$\Psi = \alpha_0(4y^2 - 2)e^{\frac{-y^2}{2}}$
n = 3	$E = \frac{7\hbar\omega}{2}$		$\Psi = \alpha_0(8y^3 + 12y)e^{\frac{-y^2}{2}}$
n = 4	$E = \frac{9\hbar\omega}{2}$		$\Psi = \alpha_0(16y^4 - 48y^4 + 12)e^{\frac{-y^2}{2}}$
n = 5	$E = \frac{11\hbar\omega}{2}$		$\Psi = \alpha_0(32y^5 - 160y^3 + 120y)e^{\frac{-y^2}{2}}$
⋮	⋮		⋮

---

2 Math Moves and Helpful Hints

The Summation Substitution: Why is replacing n with (n+2) in the power series derivation mathematically legal?

Most textbooks do not expand on the rational for this substitution. The substitution makes perfect sense, however when each term of the summation is expanded and the derivatives for each term are taken. The steps below might help with the logic behind this part of the derivation of the solution to the harmonic oscillator equation: We are given:

KAHE

$$u(y) = \sum_{0}^{\infty} \alpha_n y^n \tag{25}$$

Rewriting this summation in terms of its expansion:

$$u(y) = \alpha_0 y^0 + \alpha_1 y^1 + \alpha_2 y^2 + \alpha_3 y^3 \cdots + \alpha_n y^n \tag{26}$$

Then taking the first and second derivatives of the expanded terms, we have:

$$\frac{du(y)}{dy} = [0 + (1\alpha_1 y^{1-1}) + (2\alpha_2 y^{2-1}) \cdots + (n\alpha_n y^{n-1})] \tag{27}$$

$$\frac{d^2u(y)}{dy^2} = [0 + 0 + (2-1)(2)\alpha_2 y^{2-2} \cdots + (n-1)(n)\alpha_n y^{n-2}] \tag{28}$$

This expansion shows that the first two terms in the second derivative (equation 27 above) are zero because the coefficients are zero. The summation for the second derivative actually begins with n+2. Hence the substitution in the power series derivation above.

Hermite Polynomials: What are Hermite polynomials?

The Hermite polynomial is defined as the solution to *Hermite's Differential equation*. This polynomial is a direct result of solving the quantum harmonic oscillator differential equation. The *Hermite's Differential equation* takes the familiar form:

$$\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + 2ny = 0 \tag{29}$$

Where n is a real, non-negative number (n = 0, 1, 2, 3 …)

KAHE

Hermite polynomials form a complete orthogonal set on the interval -∞ to +∞ with respect to the function $e^{-y_{2}}$. The orthogonality relationship can be shown as such[4]:

$$\int_{-\infty}^{\infty} e^{-x^2} H_m(x) H_n(x)\,dx = \begin{cases} 0 & \mathrm{m \neq n} \\ 2^n n! \sqrt{\pi} & \mathrm{m = n} \end{cases} \tag{30}$$

With the orthogonality condition met, piecewise continuous function such as the solution to the quantum harmonic oscillator can be expressed in terms of the equation for Hermite polynomials:

$$\sum_{n=0}^{\infty} C_n H_n(x) = \begin{cases} f(x) & \text{where f(x) is continuous} \\ \frac{f(x^-)+f(x^+)}{2} & \text{where f(x) is discontinuous} \end{cases} \tag{31}$$

Where

$$C_n = \frac{1}{2^n n! \sqrt{\pi}} \int_{-\infty}^{\infty} e^{-x^2} f(x) H_n(x)\,dx \tag{32}$$

The Hermite Polynomial is graphed below[5]:

KAHE

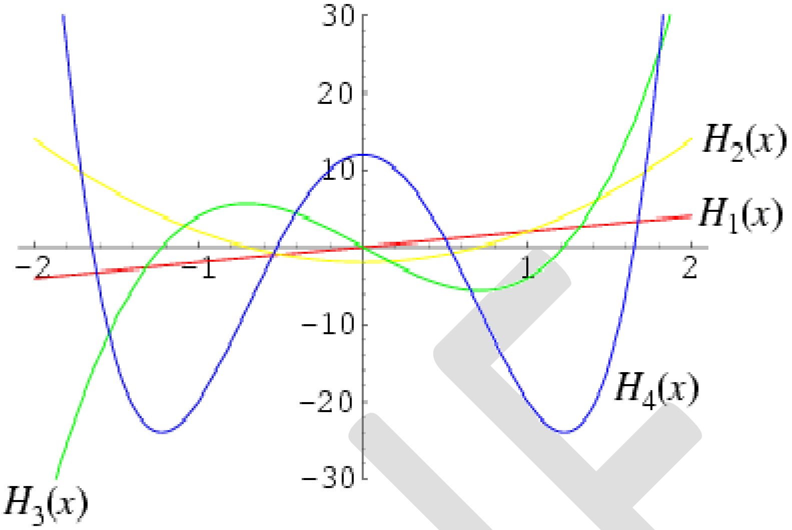


Figure 1: The Hermite Polynomial.

---

3 Solved Harmonic Oscillator Problems

1. The Schrdinger equation for the one dimensional harmonic oscillator is reduced to the following equation for the polynomial u(y):

$$\frac{d^2u(y)}{dy^2} - (2y)\frac{du(y)}{dy} + (\frac{2E}{\hbar\omega} - 1)u(y) = 0 \tag{33}$$

a. Determine the recursion relation separately for the even and the odd energy states.

b. Derive an equation for energy for both the even and the odd states from the recursion relations above.

c. Find the first three energy values from each of the equations obtained in (b).

Solution

KAHE

Part a. We begin by considering only the even states. The general solution given in the power series derivation above may be modified so that we include only these states:

$$u(y) = \sum_{0}^{\infty} \alpha_n y^{2n} \tag{34}$$

Taking the first and second derivative of u(y) we obtain:

$$\frac{du(y)}{dy} = \sum_{0}^{\infty} (2n)\alpha_n y^{2n-1} \tag{35}$$

and

$$\frac{d^2u(y)}{dy^2} = \sum_{0}^{\infty} (2n-1)(2n)\alpha_n y^{2n-2} \tag{36}$$

Putting these values for the derivative back into the differential equation:

$$\sum_{0}^{\infty} (2n-1)(2n)\alpha_n y^{2n-2} - \sum_{0}^{\infty} (2y)(2n)\alpha_n y^{2n-1} + (\frac{2E}{\hbar\omega} - 1)\sum_{0}^{\infty} \alpha_n y^{2n} = 0 \tag{37}$$

simplifying the second term we have:

$$\sum_{0}^{\infty} (2n-1)(2n)\alpha_n y^{2n-2} + (\frac{2E}{\hbar\omega} - 1 - 4n)\sum_{0}^{\infty} \alpha_n y^{2n} = 0 \tag{38}$$

Replacing n with (n+1) in the first summation, the equation can be rewritten:

$$\sum_{0}^{\infty} (2(n+1)-1)2(n+1)\alpha_{(n+1)} y^{(2(n+1)-2} + (\frac{2E}{\hbar\omega} - 1 - 4n)) \sum_{0}^{\infty} \alpha_n y^{2n} = 0 \tag{39}$$

KAHE

simplifying this:

$$\sum_{0}^{\infty}\left[2(n+1)(2n+1)\alpha_{(n+1)}+(\frac{2E}{\hbar\omega}-1-4n))\alpha_n\right]y^{2n}=0 \tag{40}$$

Again, since the coefficient must equal zero, (see RHS of equation), we can solve for $\alpha_{(n+1)}$ and obtain the recursion relation for the even states:

$$\alpha_{n+1}=\frac{4n+1-\frac{2E}{\hbar\omega}}{2(n+1)(2n+1)}\alpha_n \tag{41}$$

A similar method may be used to find the recursion relation for the odd states. This time we use a general solution of the form below so as to attain only odd states:

$$u(y)=\sum_{0}^{\infty}\alpha_n y^{2n+1} \tag{42}$$

After filling this solution into the differential equation and following the same steps as shown for the even states, one obtains the recursion relation:

$$\alpha_{n+1}=\frac{4n+3-\frac{2E}{\hbar\omega}}{2(n+1)(2n+3)}\alpha_n \tag{43}$$

Part b. As in the power series derivation above, we know that the numerator must go to zero. We can therefore, solve for the energy and obtain the equation for even states:

$$E=\frac{\hbar\omega}{2}(4n+1)=\hbar\omega\left(2n+\frac{1}{2}\right) \tag{44}$$

and the odd states:

KAHE

$$E = \frac{\hbar\omega}{2}(4n+3) = \hbar\omega\left(2n+\frac{3}{2}\right) \tag{45}$$

Part c.

The first three energy values for the even and odd states are listed below.

	Even States	Odd States
n = 0	E = $\frac{\hbar\omega}{2}$	E = $\frac{3\hbar\omega}{2}$
n = 1	E = $\frac{5\hbar\omega}{2}$	E = $\frac{7\hbar\omega}{2}$
n = 2	E = $\frac{9\hbar\omega}{2}$	E = $\frac{11\hbar\omega}{2}$

2. Find the energy levels of a particle moving in a potential field of the shape[3]

$$V(x) = \infty, (x < 0) \tag{46}$$

$$V(x) = \frac{m\omega^2}{2}x^2, (x > 0). \tag{47}$$

Solution

The first step in solving this equation is to look at the boundary conditions. As x → 0, the wave function should fall to zero. For x > 0, the wave function satisfies the differential equation for the harmonic oscillator. Since the odd wave functions for the harmonic oscillator tend toward zero as x → 0, we can conclude that the equation for the odd states in Problem 1 above is the solution to the problem:

$$E = \frac{\hbar\omega}{2}(4n+3) = \hbar\omega\left(2n+\frac{3}{2}\right) \qquad (n = 1, 2, 3, 4\cdots) \tag{48}$$

3. A Harmonic Oscillator is in the initial state: $\Psi(x,0) = \varphi_n(x)$, that is, an eigenstate of $\hat{H}$. What is $\Psi(x,t)$?[2]

KAHE

Solution

From Postulate IV of Quantum Mechanics we can show that:

$$\Psi(r,t) = e^{\frac{-it\hat{H}}{\hbar}}\Psi(r,0) \tag{49}$$

Therefore, the time-dependent wave function for the problem here is:

$$\Psi(x,t) = e^{\frac{-it\hat{H}}{\hbar}}\Psi(x,0) = \sum_n \varphi_n(x) e^{\frac{-it\hat{H}}{\hbar}} \tag{50}$$

4. Show that in the nth state of the harmonic oscillator:[2]

$$\langle x^2 \rangle = \langle \Delta x \rangle^2 \tag{51}$$

And

$$\langle p^2 \rangle = \langle \Delta p \rangle^2 \tag{52}$$

Solution

$$\langle \Delta x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 \tag{53}$$

Therefore,

$$\langle x^2 \rangle - \langle \Delta x \rangle^2 = \langle x \rangle^2 \tag{54}$$

It can be shown that because of orthogonality:

$$\langle x \rangle = \langle n|\hat{x}|n \rangle = 0 \tag{55}$$

KAHE

Therefore,

$$\langle x^2\rangle - \langle \Delta x\rangle^2 = 0 \tag{56}$$

and

$$\langle x^2\rangle = \langle \Delta x\rangle^2 \tag{57}$$

A similar case may be shown for the momentum operator

5. Using the uncertainty principles between x and p derived in Problem 3, derive the zero-point energy:

$$E_0 = \frac{1}{2}\hbar\omega \tag{58}$$

for a harmonic oscillator with natural frequency ω_0.[2]

Solution At E_0, the kinetic energy of the system equals the potential energy of the system:

$$\frac{1}{2}\frac{\langle p^2\rangle}{m} = \frac{k}{2}\langle x^2\rangle \tag{59}$$

Where

$$\omega = \sqrt{\frac{k}{m}} \tag{60}$$

From the relationship developed in Problem 3,

$$\langle x^2\rangle = \langle \Delta x\rangle^2 \tag{61}$$

KAHE

and

$$\langle p^2 \rangle = \langle \Delta p \rangle^2 \tag{62}$$

So

$$\frac{1}{2}\frac{\langle \Delta p \rangle^2}{m} = \frac{k}{2}\langle \Delta x \rangle^2 \tag{63}$$

and

$$\langle \Delta x \rangle = \frac{\langle \Delta p \rangle}{\sqrt{km}} \tag{64}$$

Therefore

$$E_0 = 2 \times \frac{1}{2}\frac{\langle \Delta p \rangle^2}{m} \tag{65}$$

Or

$$E_0 = 2 \times \frac{k}{2}\langle \Delta x \rangle^2 = k\langle \Delta x \rangle \times \langle \Delta x \rangle \tag{66}$$

Then

$$E_0 = \frac{k}{\sqrt{km}}\langle \Delta x \rangle \langle \Delta p \rangle \tag{67}$$

And

$$\langle \Delta x \rangle \langle \Delta p \rangle = \langle \frac{1}{2}\hbar \rangle \tag{68}$$

With the relationship between k and ω in equation (56),

$$E_0 = \frac{\hbar\omega_0}{2} \tag{69}$$

Harmonic Oscillator

Introduction

Many physical systems, such as a weight suspended with a spring, experience a linear restoring force when displaced from their equilibrium position. The mathematical expression for such a restoring force, F, is:

$$F = -kx$$

k is a proportionality constant called the force constant and x is the displacement from the equilibrium position. This relationship is called Hooke's law. For the spring example, k will be large for a stiff spring and smaller for springs that are weaker. Similarly, if you stretch a spring twice as far, it "springs back" with twice the force. Of course this law is valid for limited values of x. Try stretching a spring too far and you'll find that the restoring force is no longer directly proportional to displacement!

The potential energy, V, for a one-dimensional system is equal to the negative of the force integrated over x:

$$V(x) = -\int F dx = k\int x dx = \tfrac{1}{2} kx^2 + \text{constant}$$

The constant of integration depends on the physical system being modeled. For the ground state of a diatomic molecule, as modeled below, we can set it to zero.

Harmonic Oscillator Model for a Diatomic Molecule

We can model the bond in a molecule as a spring connecting two atoms and use the harmonic oscillator expression to describe the potential energy for the periodic vibration of the atoms. The potential energy, V(x), of a particle moving in one dimension is given by:

KAHE

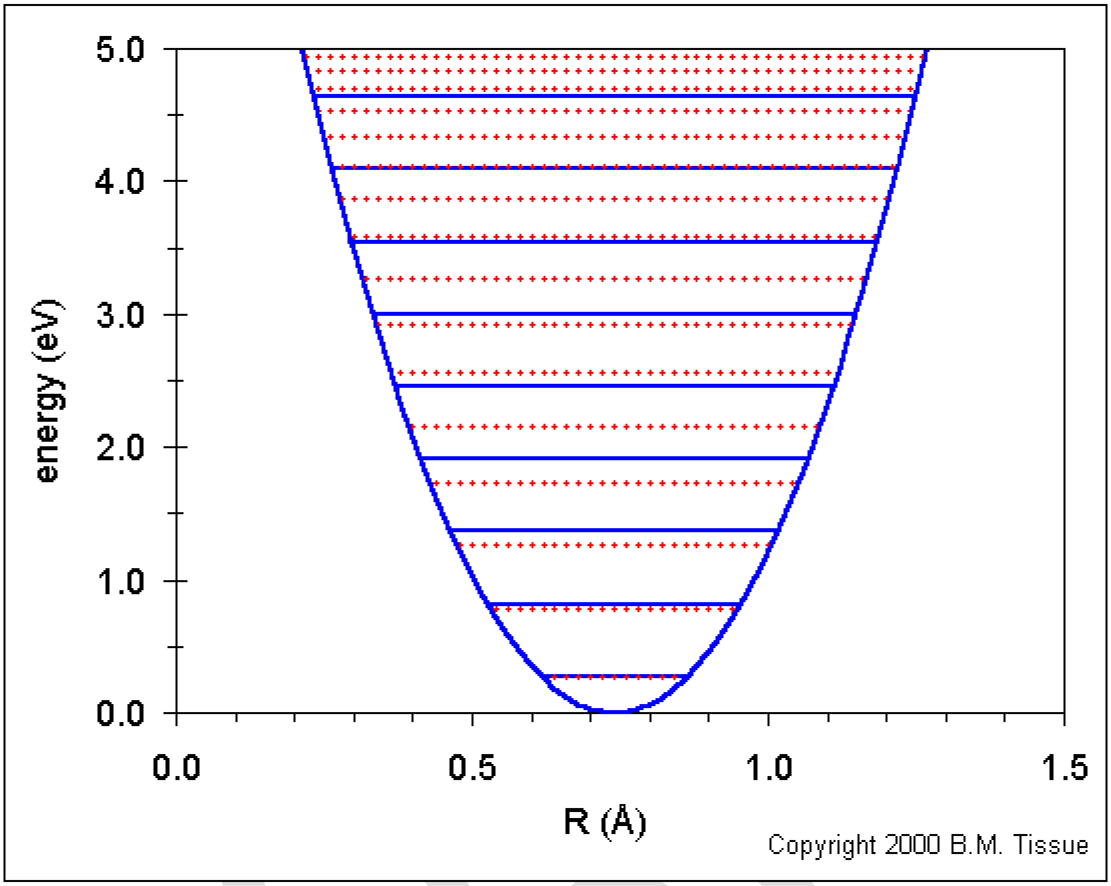
$$V(x) = \frac{1}{2} kx^2$$

where k is the force constant as above and the constant of integration is zero. We can make this expression more useful by changing x to $R-R_e$, where R is the internuclear distance (the distance between atoms) and R_e is the equilibrium internuclear distance (the bond length):

$$V(R) = \frac{1}{2} k(R - R_e)^2$$

The following figure shows the ground-state potential energy curve (called a potential well) for the H_2 molecule using the harmonic oscillator model. R_e for H_2 is 0.7412 Å. There is one obvious deficiency in the model, it does not show the energy at which the two atoms dissociate, which occurs at 4.748 eV for the H_2 molecule (1 eV = 8065.48 cm^{-1}). At some internuclear distance the atoms are far enough apart so that they do not "feel" each other. That is, they are isolated and the bond is broken. A more realistic model of the potential well of a diatomic molecule is the Morse potential, which does model the dissociation energy.

KAHE



The solid blue horizontal lines show the energy levels that are calculated using the harmonic oscillator model:

$$E_v = (v + \tfrac{1}{2})\, \nu_e$$

where v is the vibrational quantum number (v = 0,1,2,...). The v = 0 level is the vibrational ground state and is the lowest horizontal line in the plot.

ν_e is called the vibrational constant:

$$\nu_e = \tfrac{1}{2}\, \pi c \ \sqrt{({}^{k}/_{\mu})}$$

where μ is the reduced mass (m_1m_2/m_1+m_2). The simple harmonic oscillator provides a good fit to energies for the lowest energy levels, but fails at higher energies. The dotted red lines shows the energy levels calculated from:

$$E_v = (v + ½)\, \nu_e - (v + ½)^2\, \nu_e x_e + (v + ½)^3\, \nu_e y_e + \text{higher terms}$$

where v and ν_e are the same as above and x_e and y_e are the first and second anharmonicity constants respectively. These correction terms provide much better match of the calculated energies to the energies that are observed experimentally.

The Rigid Rotor

The rigid rotor is a simple model of a rotating diatomic molecule. We consider the diatomic to consist of two point masses at a fixed internuclear distance. We then reduce the model to a one-dimensional system by considering the rigid rotor to have one mass fixed at the origin, which is orbited by the reduced mass μ, at a distance r. The Schrödinger equation is (cf. McQuarrie [1], section 6.4 for a clear explanation)

$$-\frac{\hbar^2}{2I}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r) = E\psi(r) \qquad (123)$$

After a little effort, the eigenfunctions can be shown to be the spherical harmonics $Y_J^M(\theta,\phi)$, defined by

$$Y_J^M(\theta,\phi) = \left[\frac{(2J+1)}{4\pi}\frac{(J-|M|)!}{(J+|M|)!}\right]^{1/2} P_J^{|M|}(cos\theta)e^{iM\phi} \qquad (124)$$

where $P_J^{|M|}(x)$ are the associated Legendre functions. The eigenvalues are simply

$$E_J = \frac{\hbar^2}{2I} J(J+1) \tag{125}$$

Each energy level E_J is $2J+1$-fold degenerate in M, since M can have values $-J, -J+1, \ldots, J-1, J$.

REFERENCES:

1. Prasad, R. K. (2004). Quantum Chemistry (II Edition). New Delhi: New Age International Publishers Pvt. Ltd.
2. Chandra, A. K. (2002). Quantum Chemistry (IV Edition). New Delhi: Tata McGraw – Hill Publishing Company Ltd.
3. Puri, B. R., Sharma, L. R., &Pathania, M. S. (2013). Principles of Physical Chemistry (46th Edition). Jalandar: Vishal Publishing Co.

POSSIBLE QUESTIONS:

Part-A (20 x 1= 20 marks) Online Examinations

(Each Question Carry One Mark)

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 ofthe

a. **angular momentum operator** b. Lapalacian 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

1. In one dimensional box problem the potential energy of the particle outside the box is
   a. zero b. unity c. **infinity** d. fractional

2. The energy levels of the particle in the box are
   a. quantized b. randomized c. dispersed d. Not-quantized
3. 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
4. In the Hook’s law f = -kx, k is called
   a. **Force constant** b. Gas constant

   c. Boltzmann constant d. Faraday’s constant
5. 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
6. 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
7. 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

KAHE

orthogonal

8. Write the energy level for the free particle in motion
   a. En=2n-1/2 b. En=n^2 c. **En is continuous** d. En $\alpha\, n^2$

9. The shape of BeCl2 molecules is
   a. **Linear** b. Triangular planar c. Tetrahedral d. octahedral
10. Example for tetrahedral molecule
   a. BeCl2 b. boron trifluoride c**. methane** d. phosphorous pentachloride
11. 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

12. 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**

13. 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
14. Character tables are constructed using
   a. Symmetry elements b. **Orthogonality theorem**

   c. Symmetry operations d. Irreducible operations
15. The corresponding matrix for the operation E is
   a. Zero matrix b. Square matrix c. Diagonal matrix d. **Unit matrix**

16. 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)

1. Compare the classical mechanics and quantum mechanics with particle in one dimensional box.

2. Derive the equation for particle in three dimensional box and separation of variables.
3. Give an account on the applications of variation method.
4. What are the applications of Perturbation method to anharmonic oscillator and helium atom?
5. Derive Shrodinger equation for H-atom.
6. Compare the classical mechanics and quantum mechanics with particle in three dimensional box.
7. Solving Schrodinger equation for one-dimensional harmonic oscillator.
8. Discuss the quantum mechanical treatment for a harmonic oscillator.
9. For a particle in one dimensional box, show that Ψ= A Sin$\frac{n\pi}{L}x$ and E= $\frac{n2h2}{8mL2}$
10. Explain the separation of variables in Schrodinger Equation.
11. Write a short note on rigid rotator model for diatomic molecule?

PART- C (Question carries ten marks)

1. Differentiate variation method and perturbation method with an example?
2. Compare the classical mechanics and quantum mechanics with particle in three dimensional box.

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
I M.SC CHEMISTRY (2019-2021 BATCH)
SUBJECT: PHYSICAL CHEMISTRY-I (QUANTUM CHEMISTRY AND GROUP THEORY)
SUBJECT CODE: 19CHP103
MULTIPLE CHOICE QUESTIONS(EACH QUESTION CARRY ONE MARK)
UNIT-2

S. NO	**Question**	**Option A**	**Option B**	**Option C**	**Option D**	**ANSWER**
1	The solution of the problem of the rigid rotatorgives us directly the solution of the	angular momentum operator	Lapalacian operator	Hermitian operator	Position operator	angular momentum operator
2	Two atoms of mass m1 and m2 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

KAHE

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	$E_0 = ½ hv$ is the zero point energy of	Simple harmonic oscilator	Rigid rotor	Particle in one dimensional box	Particle in three dimensional box	Simple harmonic oscilator
6	$V(x) = ½ kx^2$, 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	Viscocity of the participating atoms	Bond strength between two atoms

KAHE

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	½ 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

KAHE

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 O3 has the following shape Sulfur apparently shows a valence of 6 in the molecule SF6, whereas	linear	tetrahedral	bent	equilateral triangle	bent
19	excited state of the helium atom has the term symbol	$^1S_0$	$^3S_1$	$2s_2$	He^+	$^3S_1$
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	$(3/2)a_0$	$a_0/4\pi$	$1/a_0$	$1/a_0$
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 ^1h.	The wavefunction is spherically symmetrical.	The wavefunction decreases exponentially as a function of r.	The electron's angular momentum equals ^1h.
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 -1
24	The orbital degeneracy (excluding spin) of hydrogen atom energy levels equals	n	n + 1	2n + 1	n^2	n^2

KAHE

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 SchrÄodinger 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 dfferential equations.	otherwise the atomic orbitals would violate the Pauli exclusion principle.	the Schrodinger equation is then separable into 3 ordinary dfferential 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	hk	ihk	h^2k^2	hk
32	Which of the following is NOT a solution of the differential equation "(x) + $k_2y(x) = 0$	exp(¡ikx)	exp(¡kx)	sin kx	cos kx	exp(¡kx)
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.

KAHE

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 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 figue, which of the following statement about the paticle is not correct ?	The particle will always be in a bound state	The probability of finding the particle in one 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 V0 at x =0 1. if E<V0 , wave function of the particle is zero for x>0 2. if E< V0 , wave function is not zero for x>0 3. if E> V0 , 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 polynamials 3. Hermite polynamials. 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 fo a paticle in one-dimentional 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 peturbation $H' = ax$, where a is a constant, is added to infinite squre 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-dimentional box of length l, what is the average of momentum Px for the ground state	zero	h/(2l)	h/l	h/ (2πl)	h/(2l)
43	If n represents the number of eigen states of a hydrogen atom, then its discrete energy levels are proportional to	n	n2	1/n	$1/n^2$	$1/n^2$

KAHE

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-dimentional box extending from x=-2L to x = +2L. The wave function of the particle in this state $\Psi(x) = \Psi0 \cos \pi x/4L$, where Ψ0 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	Paulis 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

KAHE

52	The electron inside the box is	Not at rest at 0^{o}K.	Not at rest at 0^{o}C	Not at rest at 298K	Not at rest at 300K	Not at rest at 0^{o}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

LECTURE NOTES

UNIT-3 (Approximation methods)

SYLLABUS

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.

KAHE

The hydrogen atom:

Schrödinger equation for hydrogen atom:

Schrödinger equation can be solved completely for hydrogen atoms as well as hydrogen type atoms, like, He^{1+} , Li^{2+} ($Z = 1$). For the other atoms only approximate solution can be achieved.

For most calculations, it is simpler to solve the wave equation if the Cartesian coordinates x , y , and z are converted to polar coordinates, r , θ , and Φ .

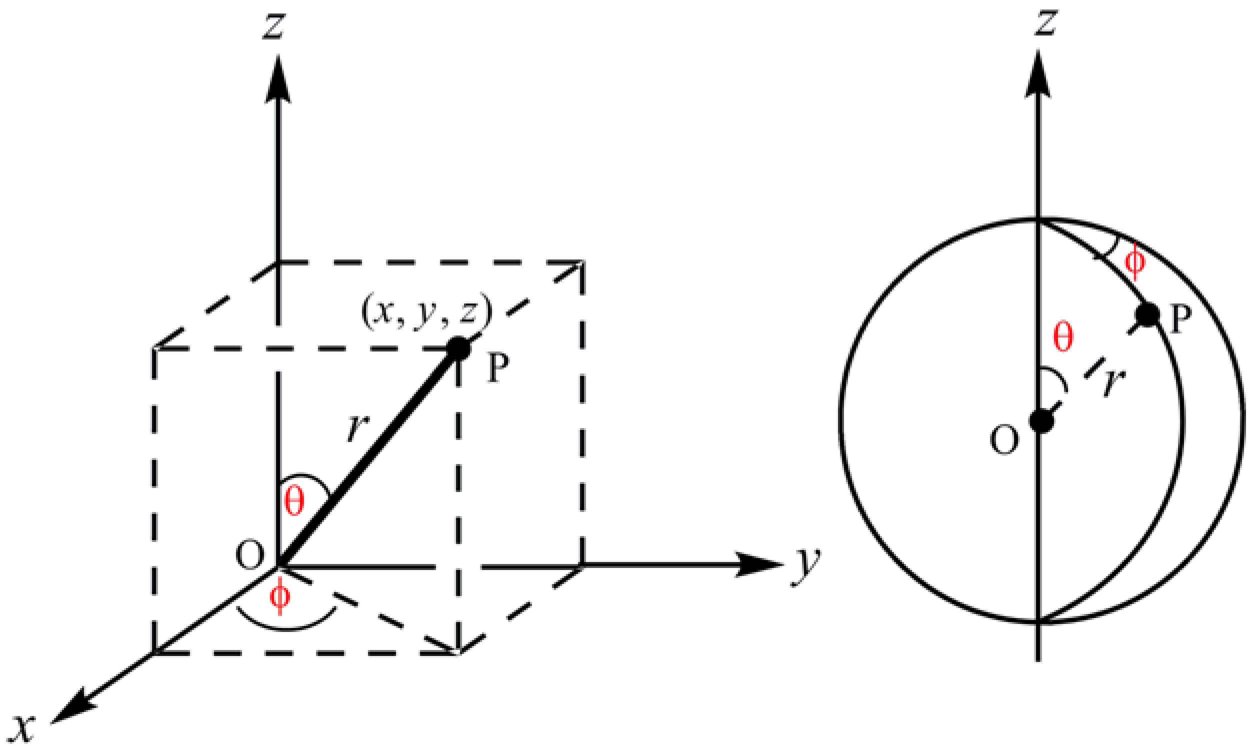


Figure 1.5. Cartesian and polar coordinates.

It can be seen from Figure 1E that two sets of coordinates are related to each other by the following relation,

$z = r \cos \theta$

$y = r \sin \theta \sin \Phi$

$x = r \sin \theta \cos \Phi$

The Schrödinger equation is written as,

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \text{(xix)}$$

Where,

$$\nabla^2\psi = \frac{\partial^2\psi}{dx^2} + \frac{\partial^2\psi}{dy^2} + \frac{\partial^2\psi}{dz^2}$$

Changing to polar coordinates, $\nabla^2\Psi$ becomes,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{r^2 sin^2\theta}\frac{\partial}{\partial\theta}\left(sin\ \theta\frac{\partial\psi}{\partial\theta}\right)$$

Now we can write equation (xix) as,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{r^2 sin^2\theta}\frac{\partial}{\partial\theta}\left(sin\ \theta\frac{\partial\psi}{\partial\theta}\right) + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \text{(xx)}$$

or,
$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{r^2 sin^2\theta}\frac{\partial}{\partial\theta}\left(sin\ \theta\frac{\partial\psi}{\partial\theta}\right) + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi \qquad \text{(xxi)}$$

(Potential energy (E_k) = V , see equation vii)

The dependence of ψ on *r* , *θ* , and *Φ* can not be shown directly with equation (xxi). Because, it would require a four dimensional graph. However, the equation in this form can be express as follows,

$$\psi = R(r).\Theta(\theta).\Phi(\phi) \qquad \text{(xxii)}$$

- *R* (*r*) is a function that depends on the distance from the nucleus. It depends on the quantum numbers *n* and *l* .
- Θ (θ) is a function of θ and depends on the quantum numbers *l* and *m* .
- Φ (Φ) is a function of Φ and depends on the quantum numbers *m* .

Therefore, equation (xxii) can be express as,

$$\psi = R(r)_{nl}.A_{ml}$$

This splits wave function into two parts which can be solved separately,

- $R(r)$ is a radial function that depends on the quantum numbers n and l .
- A_{ml} is the total angular wave function that depends on the quantum numbers m and l .

Radial part of wave functions, *R* :

The radial function R has no meaning. R^2 gives the probability of finding the electron in a small volume d v near the point at which R is measured.

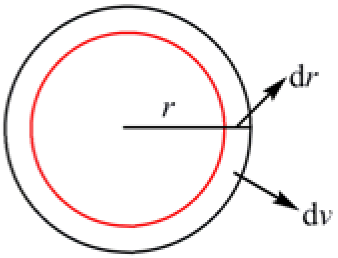


Figure 1.6. Showing volume difference

For a given value of r the total volume will be,

$$V = 4\pi r^3/3$$

We may consider that an atom is composed of thin layers of thickness d r . The volume d v for between r and r +d r will be then (Figure 1F),

$$dV = 4\pi r^2 dr$$

The probability of finding the electron in that volume will be,

$$R^2 dV = 4\pi r^2 R^2.$$

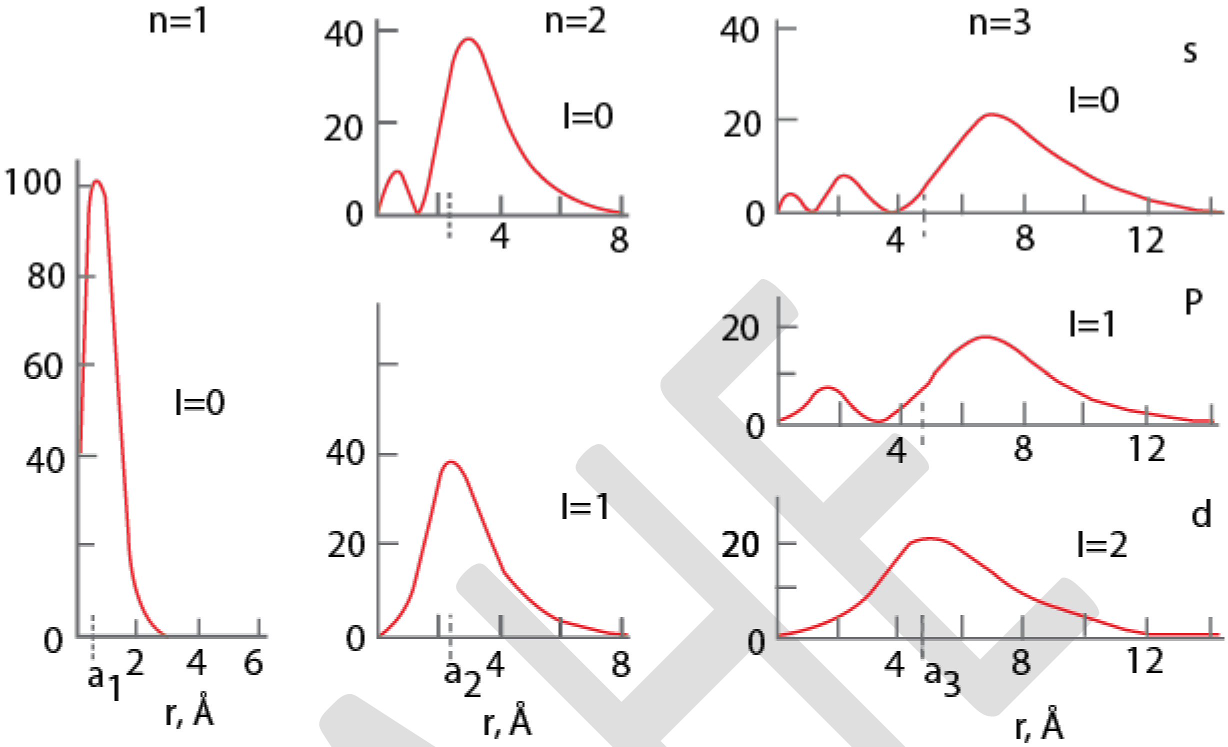
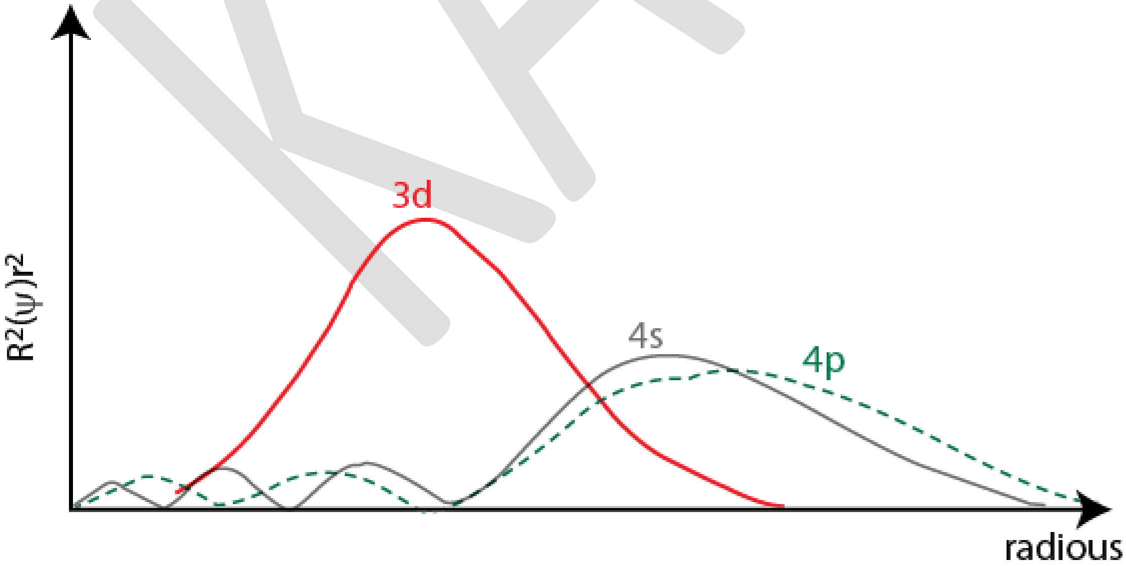


Figure 1.7. Radial probability functions for n = 1, 2,3 for the hydrogen atom. The radial density is along *y* axis.



KAHE

Figure 1.8.

Significance:

- The probability function is always positive as it involves the square of R .
- At $r = 0$, the probability of finding electron is zero. This shows no existence of electron at the nucleus.
- R is a function of n and l . Therefore, with increase in value of either n or l , the distance of finding maximum electron density form the nucleus will also increase.
- At a large value of r, R approaches to zero. Therefore, the probability of finding electron will approach to zero.
- Most probable distance increases as the principle quantum number (n) increases.
- Most probable distance decreases slightly as the subsidiary quantum number (l) increases.

Penetration:

Penetration of orbitals means their distribution into inner electronic core. For example, the radial density of 2*s* orbital spread into the curve for 1s orbital. Similarly, 3s orbital is spread into 1s, and 2s orbital. Because of this spreading electrons in 2 *s* orbital or in 3 *s* orbital will not be fully screened by the inner 1s electrons from the nucleus. The extent of penetration decreases from *s* to *f* orbitals.

$s > p > d > f$

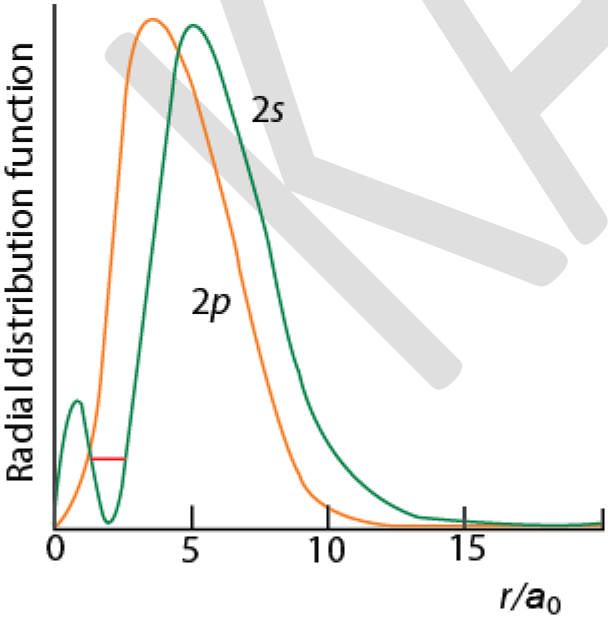


Figure 1.9. Penetration decreases from *s* to *p* as radial distribution close to nucleus for *s* is more compared to *p* .

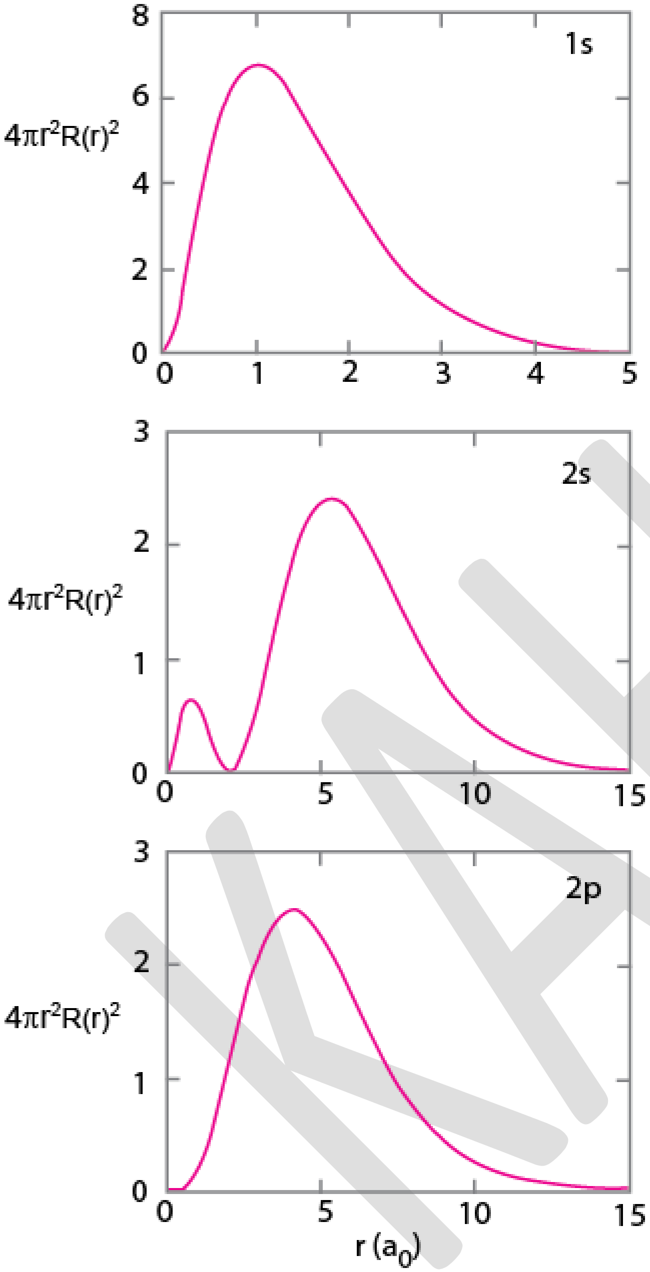


Figure 1.10. Radial distribution of 1s, 2s, and 3s orbital.

KAHE

Angular part of wave functions:

The angular parts of the wave function depend only on direction (Φ and Θ) are independent of the value of principle quantum number (n) and the distance from the radius (r). Thus, A^2 is the probability of finding an electron at a given direction Φ and Θ at any distance from the nucleus to infinity. They depend primarily on the values of l . For $l = 0$, i.e. s orbitals, the angular wave function is constant and independent of the angles θ and Φ . Therefore, this function will provide a sphere.

Angular functions for some orbitals,

s orbital	p_z orbital	dz^2
$\Theta\Phi = (1/4\pi)^{1/2}$	$\Theta\Phi = (3/4\pi)^{1/2}\cos\theta$	$\Theta\Phi = (5/16\pi)^{1/2}(3\cos^2\theta - 1)$

Here, *z* or z^2 refer the orientations of the orbitals along *z* axis. The angular wave function of the p_z orbital corresponds to two spheres whose center lies on *z* axis. The spheres touch each other tangentially at the origin. Since, cos *θ* changes sign with *θ* , the wave function will have two different sign in two different lobes.

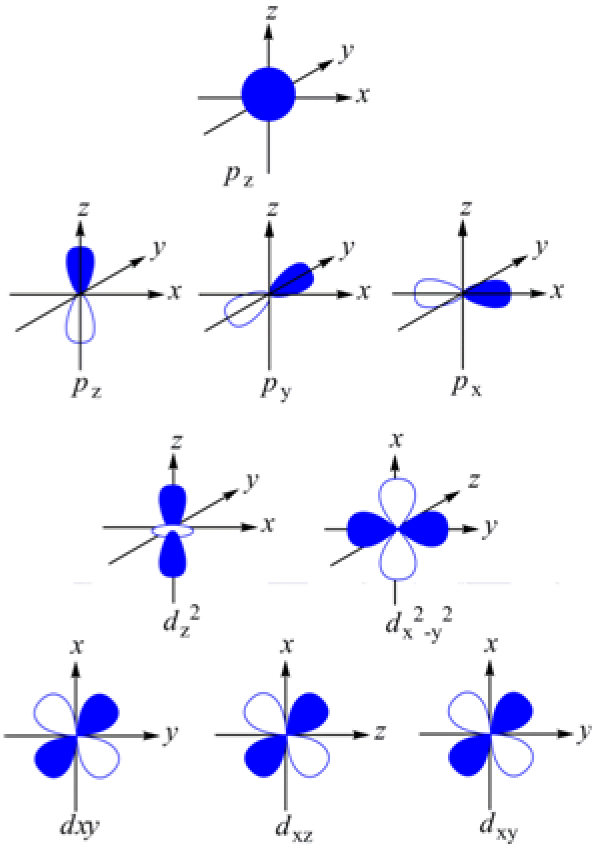


Figure 1.11. The angular part of the wave function *A* (*θ* ,. Φ) for the 1 *s* , 2 *p*, and 3 *d* orbitals for a hydrogen atom.

Similarly, there are set of five *d* orbitals (*l* = 2).

In case of *s* and *d* orbitals the wave functions have the same sign at the same distance in opposite directions from the center of symmetry. These orbitals are thus *centrosymmetric* and are said to be *gerade* . It means even and denoted as *g* . While, the wave functions for *p* orbitals have opposite signs on either side from the centre of symmetry. Therefore, they are known as *non-centrosymmetric* or ungerade orbitals. They are denoted as *u* .

Angular probability function :

The probability of finding an electron simaltanously at a distance *r* and in a given direction Φ , θ is

$\Psi^{2}{}_{r,\,\Phi,\,\theta}$

$$\psi^2_{r,\,\phi,\,\theta} = R^2(r).A^2(\phi,\,\theta)$$

The probability of finding an electron in a given direction is then A^{2} (Φ , θ).

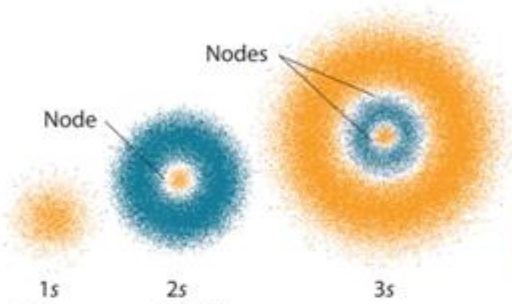
s orbital is spherical so it remains unchanged on squring, while, for *p* and *d* orbitals sign factor vanished and lobes becomes more elongated.

Difference between orbits and orbitals:

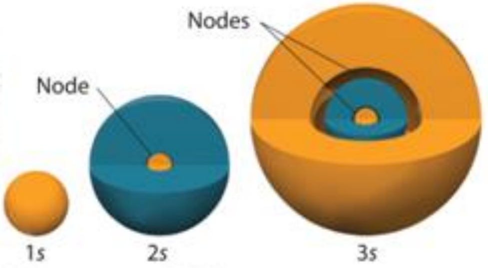
Orbit represent discreate trajectories or electrons around the positively charged nucleus. The position, momentum, and consequently, energy of an electron can be expressed precisely by using laws of newtonian mechanice assuming electron as particle.

The idea of orbital was introduced by the wavemechanical atom model. The extranuclear part has been considered as wave and follows the fundamental Schodinger wave equation. The orbital corresponds to the probability of finding an electron at a certain distance and certain direction. Hence, each orbital has definite energy, shape and described in terms of quantum numbers.

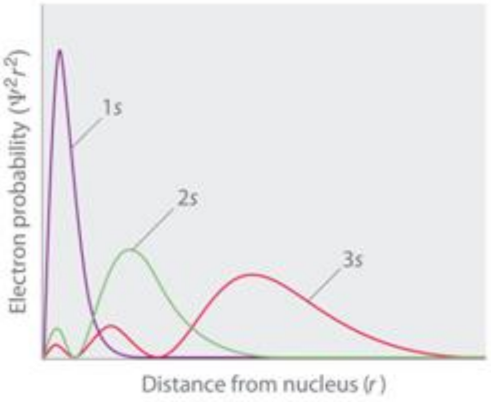
KAHE



(a) Electron probability



(b) Contour probability



(c) Radial probability

Quantum numbers:

Bohr-Sommerfeld aromic model and its later extensions, four quantum numbers (*n* , *l* , *m* , *s*) were introduced to explain the spectral features of atoms.

A. **The principle quantum number, *n* .**

This quantum number determines the energy level of an atom. The energy expressed as a function of *n* ,

$$E_t = -\frac{Z^2 m e^4}{8\varepsilon_o^2 n^2 h^2}$$

According to the above equation energy should decrease with increase of *n*value. Due to negative sign the energy also increases with increase in the value of *n* .

KAHE

B. The Azimuthal or angular momentum quantum number, *l* :

The Azimuthal or angular momentum quantum number determines the orbital angular momentum of an electron through the following relation. This specifies the shape of an atomic orbital, its bonding and bond angles.

$$L^2 = l(l+1)\hbar^2$$

l may have any integral values between 0 to (n -1). For l = 0, defines s orbital. l= 1, 2, 3, etc defines, p , d , f , etc respectively.

C. The magnetic quantum number, *m l* :

This quantum number determines the orientation of the angular momentum vector of an electron in the presence of external magnetic field along a specific axis (let consider along z axis).

$$L_Z = m_1 h$$

For a given l value m_1 will be in between + l to – l .

$$i\,.\,e\,.\,m_1 = 2\,l + 1$$

Example: for p orbital, l = 1, therefore, m_1 = +1, 0, -1. This indicates p orbital will have three different directions orientations in the presence of external magnetic field.

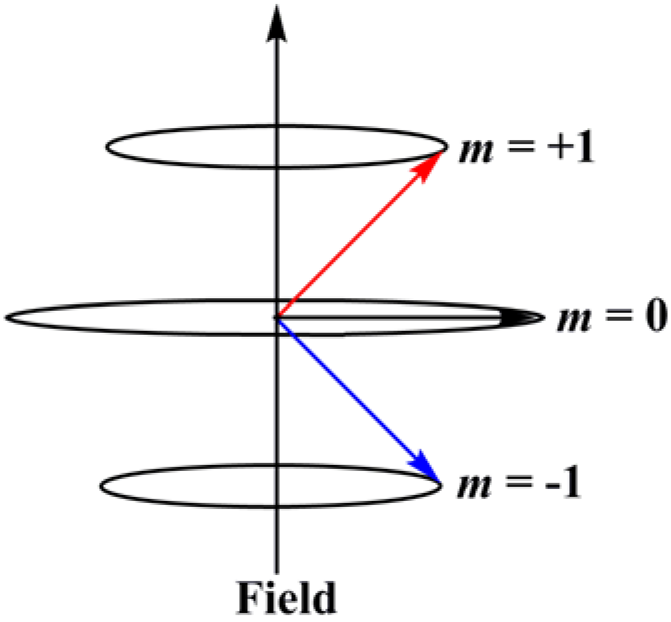


Figure 1.12. The orientation of orbital angular momentum vector in the presence of external magnetic field for $l = 1$.

(D) Spin projection quantum number, m_s :

An electron spins about its own axis. Because of this spinning an angular momentum is generated that is completely different from the orbital angular momentum. This angular momentum is expressed by spin projection quantum number (m_s).

$L_z = m_s h$

For a given s value m_s will have value in the range of +s to –s.

An electron has s = ½ spin, Hence, m_s = +1/2, -1/2

Some other examples, s = 3/2, m_s = +3/2, +1/2, -1/2, -3/2

s = 3, m_s = +3/, +2, +1, 0, -1, -2, -3

This indicates, $m_s = 2s + 1$

Table 1.3.

KAHE

n	l $0 \leq l \leq n - 1$	m_l $-l \leq m_l \leq l$	Orbital type	Total no. of orbitals $2l+1$	Maximum no of electrons $2(2l+1)$
1	0	0	*s*	1	2
2	0 1	0 +1, 0, -1	*s* *p*	1 3	2 6
3	0 1 2	0 +1, 0, -1 +2, +1, 0, -1, -2	*s* *p* *d*	1 3 5	2 6 10
4	0 1 2 3	0 +1, 0, -1 +2, +1, 0, -1, -2 +3, +2, +1, 0, -1, -2, -3	*s* *p* *d* *f*	1 3 5 7	2 6 10 14

Sequence of energy level:

Rules:

A. Orbital energies increases a ($n + l$) increases.
B. If there are two orbitals with the same value of ($n + l$), the one with the smaller n has the lower energy.

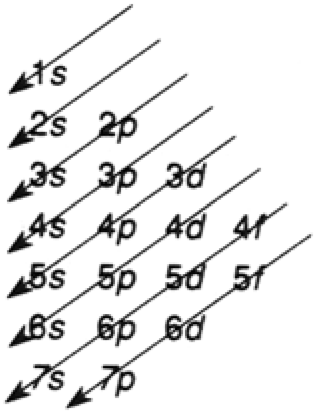


Figure 1.13. Energy levels sequence.

Many electrons atom:

Schrödinger wave equation stood good for the hydrogen atom. This wave equation become highly complicated as the number of electrons in a system increased. To avoid all the difficulties and to have the equation a simpler form a several approximations have been considered. It has been found that the radial part of the wave function changes appreciably with change in Z . The angular part of the wave function remains nearly unchanged. Therefore, the basic shape of the orbitals that depends on angular part of the wave function, are same.

Effective nuclear charge and Slater´s rule:

As the nuclear charge and the number of electrons in an atom increases, n , l also increase. It has been shown earlier that with increase of n value the probability of finding of electron at r also increases. But it does not mean there is no electron density close to the nucleus. Electron density gradually decreases to the nucleus together with appearance of nodal plane. Nodal plane is the space where the probability of finding electron is zero and the number of nodal plane is governs by the formula, $n - l -1$.

Slater proposed that nuclear charge experienced by the electrons closer to the nucleus will be greater compared to the electrons far from the nucleus. This is because of the screening of nuclear charge by the inner electron core. This is called shielding effect. The screening or shielding efficiency decreases with decreasing to penetration properties of the orbitals. Hence, it follows the sequence,

$s > p > d > f$

Because of the screening effect the actual nuclear charge (Z) may be the replaced by Z^*_{eff} which is called effective nuclear charge. It is given by the equation,

$Z^*_{\text{eff}} = Z - \sigma$

σ is sum of the shielding contribution.

Estimation of σ is governs by the following rules,

(i) The electrons are arranged in sequences of group with increase of n , and for equal n in order of l .

(1*s*), (2*s* ,2*p*), (3*s* ,3*p*), (3*d*), (4*s* ,4*p*), (4*d*), (4*f*), (5*s* ,5*p*), (5*d*), (5*f*),…….

(ii) The contribution of the electrons right to the electron that is under consideration is zero.

(iii) The contribution of each electron from same group 0.35, except 0.3 for 1*s* .

(iv) If the considered electron is under (*ns* , *np*) group, all the other electrons present at *n-1* will contribute 0.85 each and all the other at *n-2* or further left will contribute 1.00 each.

(v) If the considered electron is under (*nd*) or (*nf*) group, all the other electrons present at *n* (including *ns* , *np*) or further left will contribute 1.00 each.

Rules are in tabulated form:

Electron group	**All groups at right side**	***n* group**	**(*n*-1) Groups**	**≤ (*n*-2) Groups**
1s	0	0.3	0	0
(*ns*,*np*)	0	0.35	0.85	1.00
(*nd*) or (*nf*),	0	0.35	1.00@	1.00

@ this value will be same for *ns* , *np* .

Electron on consideration	**σ**	$Z^*_{eff} = Z - \sigma$
4*s*	(2×0.35) + (18×0.85) + (10×1.00) = 26	30-26 = 4.00
3*d*	(9×0.35) + (18×1.00) = 21.15	28-21.15 = 6.85
3*s*, 3*p*	(7×0.35) + (8×0.85) + (2×1.00) = 11.25	18-11.15 = 6.85
2*s*, 2*p*	(7×0.35) + (2×0.85) = 4.15	10-4.15 = 5.85
1*s*	0.30	2-0.30 = 1.70

The Aufbau principle:

This principle states that atoms are built up by successive addition of protons at nucleus and electron at the extra-nuclear part. The newly added electrons will occupy the available orbital of lowest energy before filling higher energy state.

The Pauli Exclusion principle:

According to this theory, no two electrons in an atom will process same set of four quantum numbers.

Hund's rules:

This rule is applied for the determination of the electronic ground state.

(i) For a given electronic configuration the term with maximum multiplicity (3 *S* + 1; *S* = spin angular momentum) will have the lowest energy.

(ii) For a given multiplicity the term with the largest *L* (angular momentum quantum number) value will occupy the lowest energy.

(iii) For a given term, in an atom with less than half - filled outer most electronic configuration, the lowest energy configuration will be with the lowest value of *J* (total angular momentum quantum number, *J* = *L* ± *S*). For more than half - filled outer most electronic configuration, the lowest energy configuration will be with the highest value of *J*.

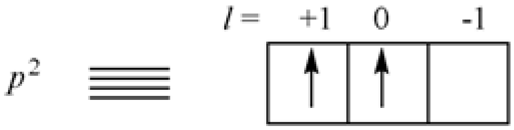
* Terms are in capital letter as they represent energy states of electronic configuration.

Example:

KAHE

$2S+1 L_J$

S = No. of unpaired electron(s)×1/2. L stands as, $L = 0$ is S, $L = 1$ is P, $L = 2$ is D, $L = 3$ is F, $L = 4$ is G, and so on. J is the vector sum of L and S. It varies as, $J = L + S$, $L + S - 1$, $L + S - 2$, ... $L - S$



S = 2 X 1/2 = 1,

Hence, 2S + 1 = 2X1+1 = 3

L = 1 + 0 = 1

Hence, symbol will be $^3P_2$, $^3P_1$, $^3P_0$ [as $J = L+S$ to $L-S$]

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. In one dimensional box problem the potential energy of the particle outside the box is

a. zero b. unity c. **infinity** d. fractional

2. The energy levels of the particle in the box are
   a. quantized b. randomized c. dispersed d. Not-quantised
3. 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
4. In the Hook's law f = -kx, k is called
   a. **Force constant** b. Gas constant
   c. Boltzmann constant d. Faraday's constant
5. The lowest energy orbital for the ammonia molecule is designated
   a. 1s b. 1σg c. **1a1** d. C3v
6. The benzene molecule C6H6 has how many vibrational modes a. 6 b. 12 c. 24 d. **30**
7. 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
8. The energy level belongs to En=2n-1/2
   a. **Harmonic oscillator** b. Hydrogen atom
   c. particle in a box d. free particle in motion
9. The shape of BeCl2 molecules is
   a. **Linear** b. Triangular planar c. Tetrahedral d. octahedral
10. Example for tetrahedral molecule
    a. BeCl2 b. boron trifluoride c**. methane** d. phosphorous pentachloride
11. 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
12. 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**
13. For a pyramidal molecule with point group C3v the number of theoretically

KAHE

predicted IR fundamental bands

a. **Three** b. Four c. Five d. Six

14. 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

15. In case of molecules with a centre of symmetry the vibrational modes are anti-symmetricto centre of inversion are

a. IR inactive b. **IR active** c. Raman inactive d. Raman hyper active

16. 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?

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? It this 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 (question carries ten marks)

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

KAHE

KAHE

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
I M.SC CHEMISTRY (2019-2021 BATCH)
SUBJECT: PHYSICAL CHEMISTRY-I (QUANTUM CHEMISTRY AND GROUP THEORY)
SUBJECT CODE: 19CHP103
MULTIPLE CHOICE QUESTIONS(EACH QUESTION CARRY ONE MARK)

UNIT-3		**Option A**	**Option B**	**Option C**	**Option D**	**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

KAHE

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	$10\ \pi^2h^2/mL^2$	$10\pi^2h^2/3mL^2$	$11h^2\pi^2/mL^2$	$11h^2\pi^2/mL^2$	$10\ \pi^2h^2/mL^2$
11	The ratio of the reflected to the incident amplititude A_R/A_0	$1-\ A_T/A_0$	√(1-T) in magnitude	a real negative number	1+ AT/A0	$1-\ A_T/A_0$
12	The expected value of kinetic enegy in terms of h,k and m is	$\hat{E}_K= h/2m$	$\hat{E}_k= h^2k^2/m$	$\hat{E}_k=$ h2k/2m	$\hat{E}_k=$ h2k2/2m	$\hat{E}_k=$ h2k2/2m
13	Time relation between Ψ and E_k is	$\hat{E}_k\Psi= h^2/2m\ \Psi$	$\hat{E}_k\Psi= h^2k^2/2m\ \Psi$	$\hat{E}_k\Psi= h^2k^2/m\ \Psi$	$\hat{E}_k\Psi= h^2k^2/m^2\ \Psi$	$\hat{E}_k\Psi= h^2k^2/2m\ \Psi$

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 $\Psi=(^3\Psi_1 +^4\Psi_2)/5$ 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 zeo	Can be chosen to be real
17	probability of least probable isotopmer is	$(0.00015)^2$ x0.011	$(0.00015)^2$ x0.989	$(0.99985)^2$x0.011	0.99985x0.00015x0.989	$(0.00015)^2$ x0.011
18	Least probable isotopomer is	D-^{13}C-D	^{1}H-^{13}C-^{1}H	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≥1	a=0	a=0 t0 1	a = -1 to +1	a=0
21	Value of <H> is	greater than E_0	greater than and equal to E_0	lesser than E_0	Lessor than and equal to E_0	greater than and equal to E_0

KAHE

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 $E_n \alpha n^2$	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	$E_n \alpha n^2$	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	$E_n \alpha n^2$	$E_n=n^2$

KAHE

KAHE

31	Write the energy level for the Hydrogen atom	E_n=2n-1/2	E_n is continuous	$E_n=n^2$	E_n α n^2	E_n α 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 α 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 $c(hω/k)^2$	1/2 c $(hω/k)^2$	C hω/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/α,qEa	qEa/α,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&O]	[1&1]	[A*/E_1-E_2&O]
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

KAHE

39	An unperturbed two level system has energy eigen values E_1 and E_2 and eigen functions [1&0] and [0&1] when peturbed its Hamiltonian is represented by the first order corection to E1 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 $\Psi(\theta,\phi)=1/\sqrt{20}$ [3Y02 + $\sqrt{7}$Y02 - 2Y12], the probability of finding the system in a state with m=0 is	4/5	1/5	2/5	3/5	4-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 $\Psi = \sqrt{2/L}\cos \pi x/Le^{-Et/h}$, then <x> 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=o to x=9. 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_o /2 coming from left encounters a potential -3v_o/2 at x=0 V(x)=o for x<a and V(x)=-3vo/2 for x>a,transmission coefficient is	1/2	2/3	4/9	8/9	4-Sep
46	Consider a particle in one dimensional box between x=o and x=a V(x) ={=∞ for x<o or x>a=o for o<x<a when is the pobability that it will be found in the region a/4<x<3a/4?	1/2	1/2+1/π	1/4+2/π	1/4+1/π	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>o?	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 etending 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)	$10h^2/ma^2$	$8h^2/ma^2$	$15h^2/4ma^2$	$15h^2/2ma^2$	$15h^2/4ma^2$

KAHE

49	what is the faction of beam reflected fom the step barrrier of V_0 if enegy ofelectron E with E> V_0 and width of barrier is infinite,is given by	E/V_O	$E-V_O/V_O$	$E-V_O/2V_O$	$E+V_O/E$	$E-V_O/V_O$
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 disssociation 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 C6H6 has how many vibrational modes	6	12	24	30	30
53	The lowest energy orbital for the ammonia molecule is designated	1s	$1\sigma_g$	$1a_1$	C_{3v}	$1a_1$

KAHE

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

KAHE

LECTRUE NOTES

UNIT-IV **Symmetry elements and Matrices**

SYLLABUS

UNIT-IV ***Symmetry elements and Matrices***

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.

KAHE

Symmetry can help resolve many chemistry problems and usually the first step is to determine the symmetry. If we know how to determine the symmetry of small molecules, we can determine symmetry of other targets which we are interested in. Therefore, this module will introduce basic concepts of group theory and after reading this module, you will know how to determine the symmetries of small molecules.

Introduction

Symmetry is very important in chemistry researches and group theory is the tool that is used to determine symmetry. Usually, it is not only the symmetry of molecule but also the symmetries of some local atoms, molecular orbitals, rotations and vibrations of bonds, etc. that are important.

For example, if the symmetries of molecular orbital wave functions are known, we can find out information about the binding. Also, by the selection rules that are associated with symmetries, we can explain whether the transition is forbidden or not and also we can predict and interpret the bands we can observe in Infrared or Raman spectrum.

Symmetry operations and symmetry elements are two basic and important concepts in group theory. When we perform an operation to a molecule, if we cannot tell any difference before and after we do the operation, we call this operation a *symmetry operation*. This means that the molecule seems unchanged before and after a symmetry operation. As Cotton defines it in his book, when we do a symmetry operation to a molecule, every points of the molecule will be in an equivalent position.

Symmetry Elements

For different molecules, there are different kinds of symmetry operations we can perform. To finish a symmetry operation, we may rotate a molecule on a line as an axis, reflect it on a mirror plane, or invert it through a point located in the center. These lines, planes, or points are called symmetry elements. There may be more then one symmetry operations associated with a particular symmetry

Identity E

The molecule does not move and all atoms of the molecule stay at the same place when we apply an identity operation, E, on it. All molecules have the identity operation. Identity operation can also be a combination of different operations when the molecule returns to its original position after these operations are performed.[1] This will be demonstrated later.

Proper Rotations and Cn axis

C_n generates n operations, whose symbols are C_n, C_n^2, C_n^3, C_n^4,…, E (=C_n^n). However, we usually write them in another way. Table 1.2 shows the way we write the 6 operations generated by proper rotation C_6. From this table, we can see that the symbols of the 6 rotations generated by C_6 are C_6, C_3, C_2, C_3^2, C_6^5, E.One molecule can have many proper axes and the one with the largest n is called ***principle axis***.

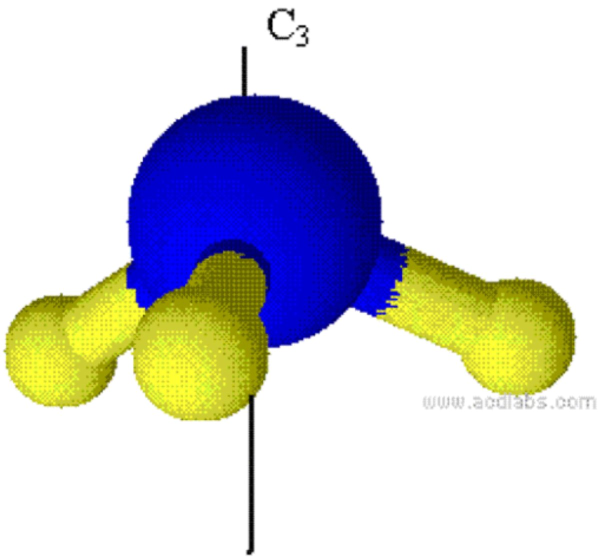
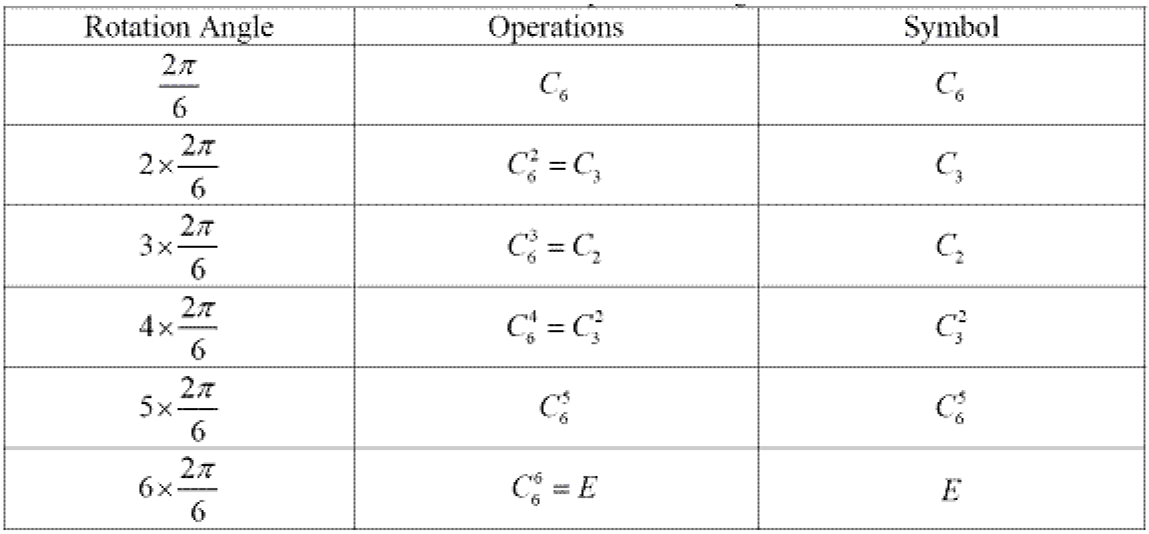


Table 1.2 C_6 axis and operations it generates



Rotation Angle	Operations	Symbol
$\frac{2\pi}{6}$	C_6	C_6
$2\times\frac{2\pi}{6}$	$C_6^2 = C_3$	C_3
$3\times\frac{2\pi}{6}$	$C_6^3 = C_2$	C_2
$4\times\frac{2\pi}{6}$	$C_6^4 = C_3^2$	C_3^2
$5\times\frac{2\pi}{6}$	C_6^5	C_6^5
$6\times\frac{2\pi}{6}$	$C_6^6 = E$	E

Reflection and mirror plane σ

Take NH_3 for an example. There are 3 mirror planes in molecule NH_3. When we do a reflection through a mirror plane, molecule NH_3 dose not change (Figure 1.2).

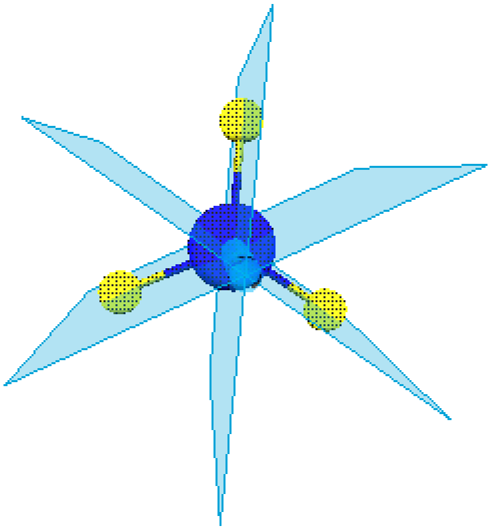


Figure 1.2 A mirror plane of NH_3.

There are three different kinds of mirror plane, σvσv, σhσh, and σdσd. The mirror plane that contains the principle axis is called σvσv.The mirror plane that perpendicular to the principle axis is called σh.2 Figure 1.3 shows σvσv, σhσh, and σdσd in PtCl2−4PtCl42−.

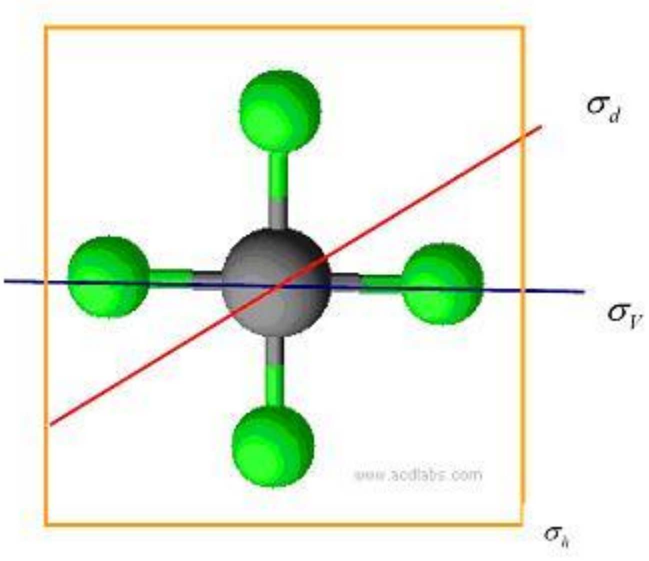


Figure 1.3 σvσv, σhσh, and σdσd of $PtCl_4^{2-}$.This picture is drawn by ACD Labs 11.0.

When mirror plane is operated n times, we have[1]

$$\sigma^n = \begin{cases} E(when\ n\ is\ even) \\ \sigma(when\ n\ is\ odd\ ) \end{cases}$$

Inversion and inversion center i

In a molecule, if we can find a point, on the straight line through which we can find a pair of same atoms on both side of this point, we call this molecule has an inversion center. The inversion center, *i*, is not necessarily on an atom of the molecule.[1]Figure 1.4 shows the inversion center of C2H4Cl2C2H4Cl2.When inversion is operated n times, we have[1]

$$i^n = \begin{cases} E(when\ n\ is\ even) \\ i(when\ n\ is\ odd\ ) \end{cases}$$

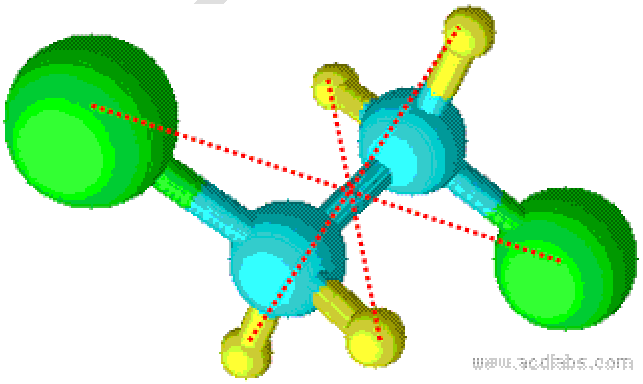


Figure 1.4 Inversion center of $C_2H_4Cl_2$.

Improper Rotations and S_n axis

Improper rotation is a combination of two operations, proper rotation C_n and reflection ?. Figure 1.5 shows the improper rotation operation in CH_4.

Table 1.3 and table 1.4 show the operations generated by S_6 and S_5 axes separately. The 6 operations generated by S_6 axis are S_6, C_3, i, C_3^2, S_6^5 and E. And the 10 operations generated by S_5axis are S_5, C_5^2, S_5^3, C_5^4, ?, C_5, S_5^7, C_5^3, S_5^9 and E.[1]Since S_1= σhσh and S_2=$\sigma_h C_2$=i, the order of improper rotation, n, must always be larger than 2. And generally, when n is even, there are n operations {S_n^1, S_n^2, ..., S_n^n}, while when n is odd, there are 2n operations {S_n^1, S_n^2, ..., S_n^{2n}}. And we have[1]

$$S_n^m = \begin{cases} \sigma C_n^m \,(when\ m\ is\ odd) \\ C_n^m \ (when\ m\ is\ even\ ) \end{cases}$$

$$S_n^n = \begin{cases} \sigma \ (when\ m\ is\ odd) \\ E(when\ m\ is\ even\ ) \end{cases}$$

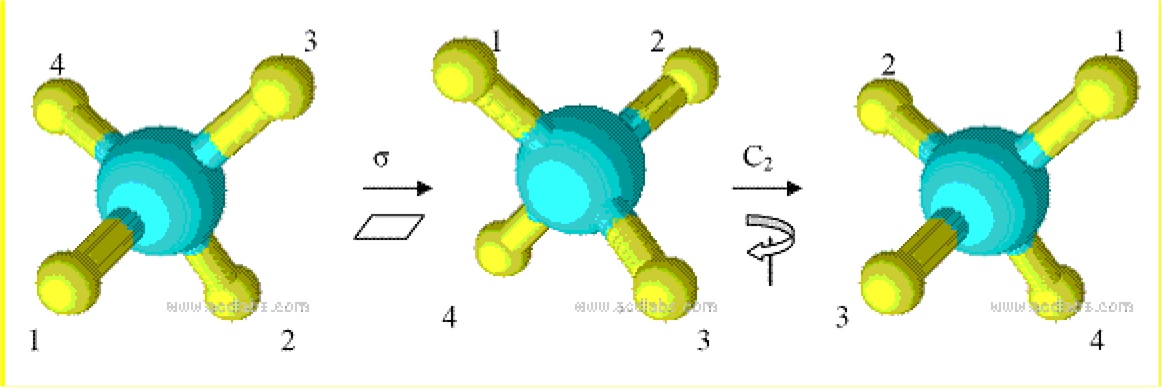
Table 1.3 S_6 axis and operations it generates

Rotation Angle	Operations	Symbol
$\frac{2\pi}{6}$	$S_6 = \sigma C_6$	S_6
$2\times\frac{2\pi}{6}$	$S_6^2 = C_6^2 = C_3$	C_3
$3\times\frac{2\pi}{6}$	$S_6^3 = S_2 = i$	i
$4\times\frac{2\pi}{6}$	$S_6^4 = C_3^2$	C_3^2
$5\times\frac{2\pi}{6}$	$S_6^5 = \sigma C_6^5$	S_6^5
$6\times\frac{2\pi}{6}$	$S_6^6 = E$	E

Table 1.4 S_5 axis and operations it generates

Rotation Angle	Operations	Symbol
$\frac{2\pi}{5}$	$S_5 = \sigma C_5$	S_5
$2\times\frac{2\pi}{5}$	$S_5^2 = C_5^2$	C_5^2
$3\times\frac{2\pi}{5}$	$S_5^3 = \sigma C_5^3$	S_5^3
$4\times\frac{2\pi}{5}$	$S_5^4 = C_5^4$	C_5^4
$5\times\frac{2\pi}{5}$	$S_5^5 = \sigma$	σ
$6\times\frac{2\pi}{5}$	$S_5^6 = C_5$	C_5
$7\times\frac{2\pi}{5}$	$S_5^7 = \sigma C_5^2$	S_5^7
$8\times\frac{2\pi}{5}$	$S_5^8 = C_5^3$	C_5^3
$9\times\frac{2\pi}{5}$	$S_5^9 = \sigma C_5^4$	S_5^9
$10\times\frac{2\pi}{5}$	$S_5^{10} = E$	E

Figure 1.5 Improper rotation operation S_4 in CH_4



Symmetry Point Groups

For a molecule, all the symmetry operations that can be applied to the molecule have all the properties of a group. Therefore, before we introduce the symmetry point groups, the concept and properties of a group will be introduced first. When some elements have a certain kind of relationships and can be related to each other by these relationships, these elements can form a *group*.

Closure

If two elements A and B are in the group G, then the multiplicity of these two elements, C, is also in this group. It can be expressed as

Associativity

All the elements in the group must satisfy the law of associativity, which can be expressed as

$$(AB)C=A(BC)$$

Identity

The group must contain such an element E that

$$ER=RE=R$$

In group theory, it refers to the operation identity E. Because any molecule or substance must at least have the symmetry element E.

Inverses

If A is an element in group G, there must be another element A^{-1} in group G that satisfies $AA^{-1}= A^{-1}A=E$. Usually we can write A^{-1} as B. It can be expressed as

$$\text{If AG and } AA^{-1}= A^{-1}A=E \text{ then } A^{-1}=B=G$$

Group Multiplication Tables

If there are n elements in a group G, and all of the possible n^2 multiplications of these elements are known, then this group G is unique and we can write all these n^2 multiplications in a table called group multiplication table. All the symmetry operations of a molecule can be written in the form of group multiplication table. There is a very important rule about group multiplication tables called *rearrangement theorem*, which is that every element will only appear once in each row or column.[1]In group theory, when the column element is A and row element is B, then the corresponding multiplication is AB, which means B operation is performed first, and then operation A follows.[1]

Table 2.1 Group multiplication table[1]

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

Subgroups

From table 2.1 above, we can find several small groups in the group multiplication table. For example,

G_2	E	A
E	E	A
A	A	E

In the same way, there are also many several small groups with orders 1, 2, 3 respectively. These small order groups that can be found in a higher order group are called *subgroups*. The number of elements in a group is called the order of a group, using a symbol *h*. The number of elements consist a subgroup is called the order of a subgroup, using a symbol *g*. From the previous two examples, we have[1],

$$h/g=k \text{ (}k\text{ is a whole number)}$$

Since the symmetry point group have all the properties of a group, there are also several subgroups that we can find in a perticular symmetry point group. And sometimes we just use symmetry opertaions in one subgroup to apply to a system instead of using all the symmetry operations in the group, which can significantly simplify the calculations.

Classes

Class is another important concept in group theory which provides a way to simplify the expression of all the symmetry operations in a group. This means that we do not have to write down all the symmetry operatoins in a group but combine some related operations instead. The followin part will introduce the concept of classes and how to divide a group into classes.

Similarity transformation and conjugate:

A and B are two elements in a group, X is any elements in this group. If

$$X-1AX=B\text{(Group Theory.1)}$$

Then we can say the relationship of A and B is similarity transformation. A and B are conjugate.[1] Conjugate elements have three properties[1]:

a. Every element is conjugate with itself.

$$A=X-1AX\text{(Group Theory.2)}$$

b. If A is conjugate with B, then B is conjugate with A.

$$\text{If}A=X-1BX,\text{then } B=Y-1AY\text{(Group Theory.3)}$$

If A is conjugate with B and C, then B is conjugate with C.

$$\text{If}A=X-1BX \text{ and } A=Y-1CY,\text{then}B=Z-1CZ\text{(Group Theory.4)}$$

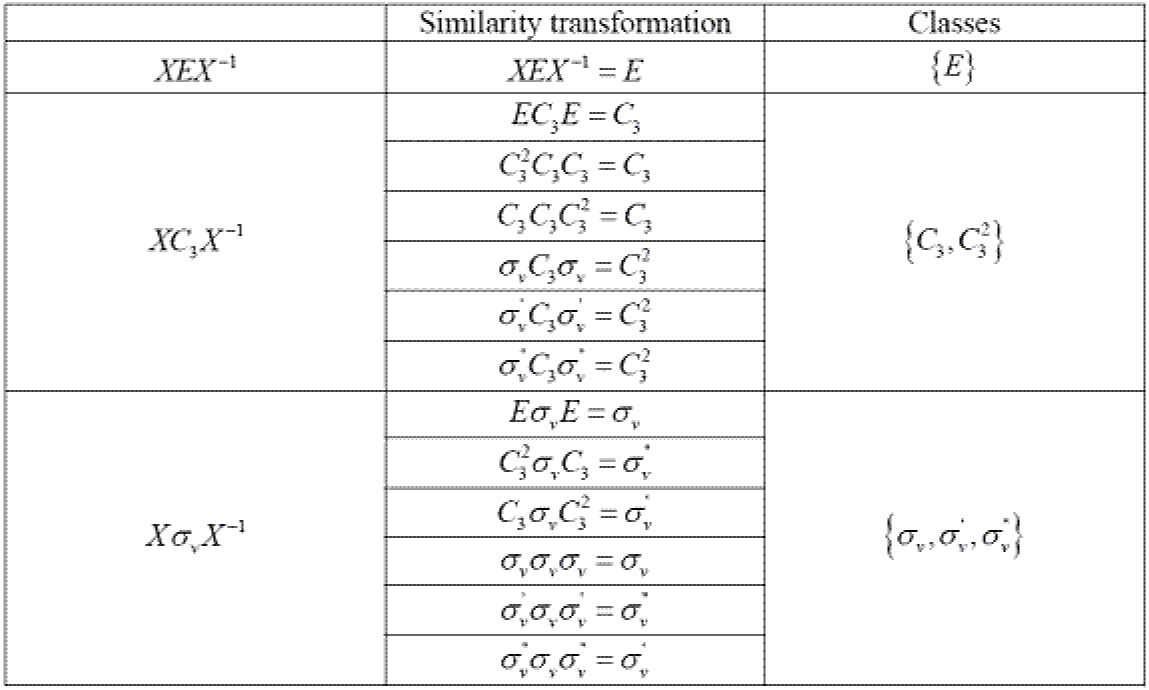
Classes

Now we can define a class. A class of a group is defined as all the elements in the group that are conjugated to each other.[1] To determine the classes of a group, we need to apply similarity transformation to the elements in the group until all the elements are grouped into smaller sets. For example, there are four elements in a group: $\{E, C_2, \sigma_v, \sigma_v'\}$

$$X= E, C_2, \sigma v\sigma v, \sigma v\sigma v' \ X^{-1}= E, C_2, \sigma_v, \sigma_v'$$

Because we always have $XEX^{-1}=E$, {E} is always a class for any point group. Then, apply similarity transformation to other elements in the group until all the elements are classified in smaller sets. Table 2.3 shows how the elements are classified in to classes.

Table 2.4 Classes six order group



	Similarity transformation	Classes
XEX^{-1}	$XEX^{-1} = E$	$\{E\}$
XC_3X^{-1}	$EC_3E = C_3$	$\{C_3, C_3^2\}$
	$C_3^2C_3C_3 = C_3$	
	$C_3C_3C_3^2 = C_3$	
	$\sigma_vC_3\sigma_v = C_3^2$	
	$\sigma_v'C_3\sigma_v' = C_3^2$	
	$\sigma_v''C_3\sigma_v'' = C_3^2$	
$X\sigma_vX^{-1}$	$E\sigma_vE = \sigma_v$	$\{\sigma_v, \sigma_v', \sigma_v''\}$
	$C_3^2\sigma_vC_3 = \sigma_v''$	
	$C_3\sigma_vC_3^2 = \sigma_v'$	
	$\sigma_v\sigma_v\sigma_v = \sigma_v$	
	$\sigma_v'\sigma_v\sigma_v' = \sigma_v''$	
	$\sigma_v''\sigma_v\sigma_v'' = \sigma_v'$	

Therefore, there are three classes in group C_{3v}: {E}, $\{C_3, C_3^2\}$ and $\{ \sigma_v, \sigma_v', \sigma_v'' \}$.

Significance of classes of a group

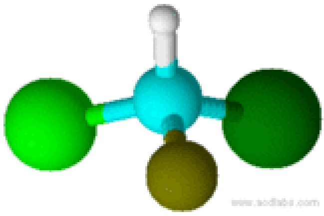
In the same class of a group, the operations can be converted to each other by an operation. The operations in the same class are called *equivalent operations*. And a class of a symmetry group is a group of equivalent operations. This gives a simpler way to express the operations in a group.[1]For example, for operations in the six order group above, table 2.5 shows the new way to express these operations.

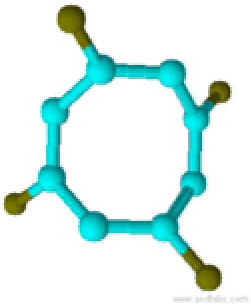
Table 2.5 Ways to express operations in six order group

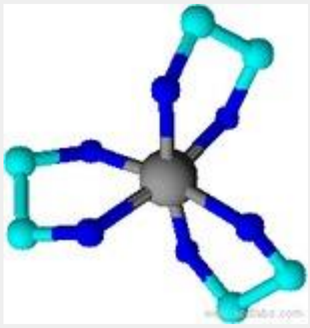
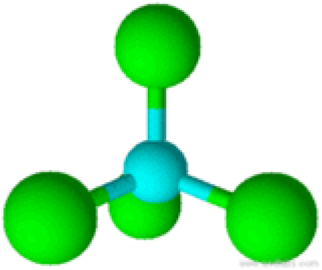
Operations	Classes	New notations
E	$\{E\}$	E
C_3	$\{C_3, C_3^2\}$	$2C_3$
C_3^2		
σ_v	$\{\sigma_v, \sigma_v', \sigma_v''\}$	$3\sigma_v$
σ_v'		
σ_v''		

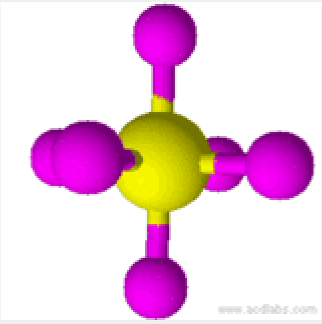
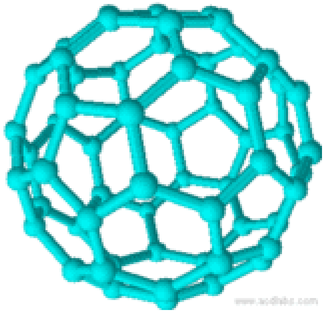
Symmetry Point Groups

As what mentioned above, all the symmetry operations of a molecule as a group can be written in the form of group multiplication table and they obey all the properties of a group. This group is called *symmetry point group*. It is called point group for two reasons. First reason is that this group have all the properties of a group. Second reason is that all the symmetry operations are related to a fixed point in the molecule, which is not necessarily to be an atom of the molecule. According to the symmetry of molecules, they can be classified as symmetry point groups.[1]To determine the symmetry point group of a molecule is very important, because all symmetry related properties are dependent on the symmetry point group of the molecule. Symmetry point groups can be divided into 5 classes which are summarized below and the they are described in details here (symmetry point groups).[1,6]

	Point groups	Symmetry Elements	Order	Example
Nonaxial	C_1	E	1	 HCFBrCl

	Point groups	Symmetry Elements	Order	Example
	C_i	E, i	2	$C_2H_2F_2Cl_2$
	C_s	E, ?	2	CH_2BrC
Cyclic	C_n	E, C_n	n	$C_2H_4Cl_2$
	C_{nh}	E, C_n, nσvσv	2n	NH_3
	C_{nv}	E, C_n, σ_h, S_n	2n	$C_2H_2F_2$
	S_n	E, S_n	n	 1,3,5,7 -tetrafluoracyclooctatetrane

	Point groups	Symmetry Elements	Order	Example
Dihedral	D_n	E, C_n, nC_2 (?C_n)	2n	 $[Co(en)_3]^{3+}$.
	D_{nh}	E, C_n, σ_h, nC_2 (?C_n)	4n	Benzene
	D_{nd}	E, C_n, σ_d, nC_2 (?C_n)	4n	C_2H_6
Polyhedral	T_d	E, $3C_2$, $4C_3$, $3S_4$, $6\sigma_d$	24	 CCl_4

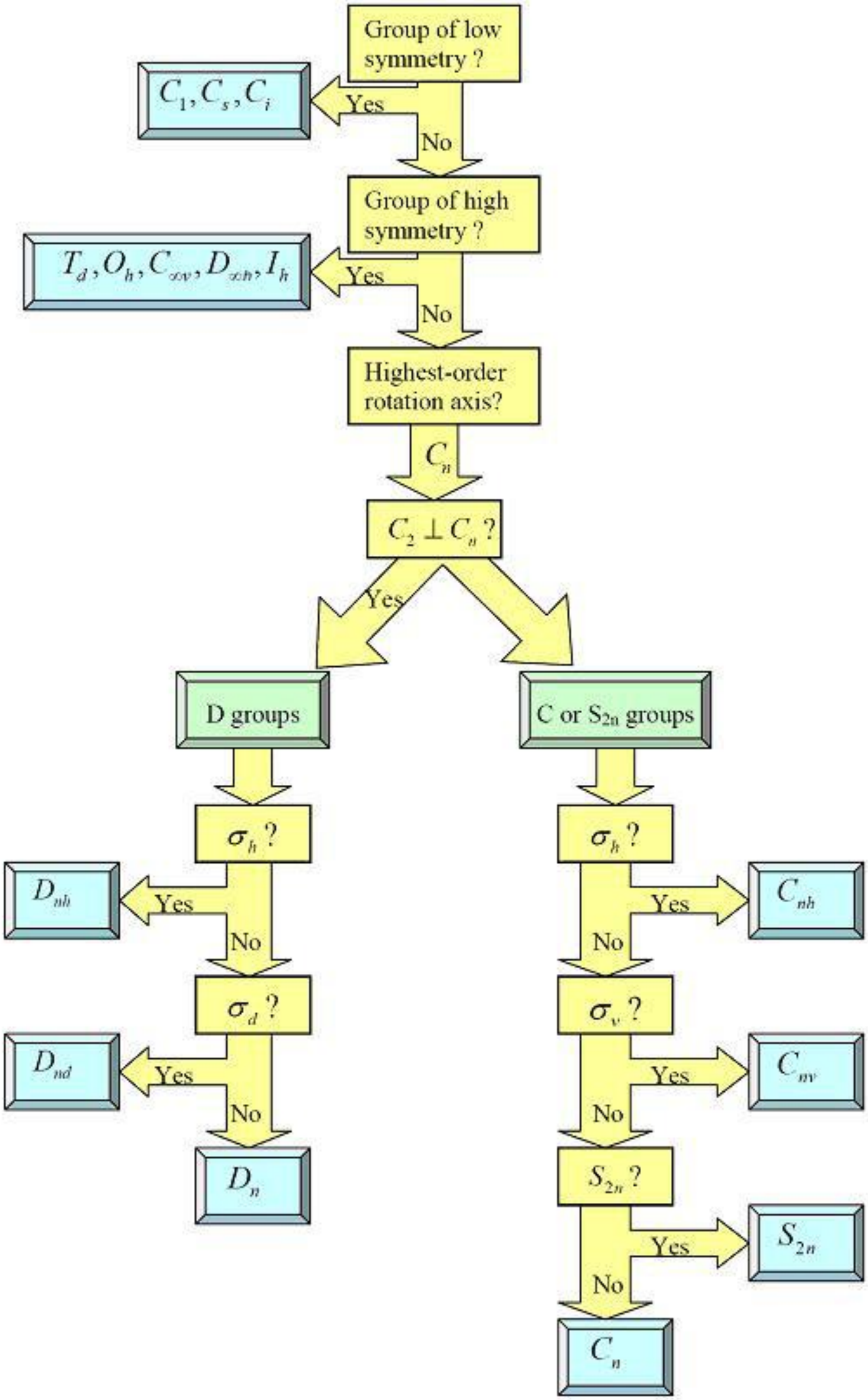
	Point groups	Symmetry Elements	Order	Example
	O_h	E, $3S_4$, $3C_4$, $6C_2$, $4S_6$, $4C_3$, $3\sigma_h$, $6\sigma_d$, i	48	 SF_6
	I_h	E, $6S_{10}$, $10S_6$, $6C_5$, $10C_3$, $15C_2$, 15?	120	 C_{60}
Linear	$C_{\sigma v \sigma v}$	E, $C_?$, σ_v	?	HCl

	Point groups	Symmetry Elements	Order	Example
	$D_{\sigma h \sigma h}$	E, $C_?$ σ_v , σ_h, i, ?C_2	?	O_2

Determination of symmetry Point Groups

Determination of symmetry point group of a molecule is the very first step when we are solving chemistry problems. The symmetry point group of a molecule can be determined by the following flow chart[7].

Table 2.12 Flow chart to determine point group


Group of low symmetry ?
C_1, C_s, C_i
Yes
No
Group of high symmetry ?
$T_d, O_h, C_{\infty v}, D_{\infty h}, I_h$
Yes
No
Highest-order rotation axis?
C_n
$C_2 \perp C_n$?
Yes
D groups
C or S_{2n} groups
σ_h ?
D_{nh}
Yes
No
σ_d ?
D_{nd}
Yes
No
D_n
σ_h ?
Yes
C_{nh}
No
σ_v ?
Yes
C_{nv}
No
S_{2n} ?
Yes
S_{2n}
No
C_n

Now, using this flow chart, we can determine the symmetry of molecules. However, to further determine the symmetry properties of something such as molecular orbitals, vibrational modes, etc. we need character tables which will be introduced next.

Character Tables

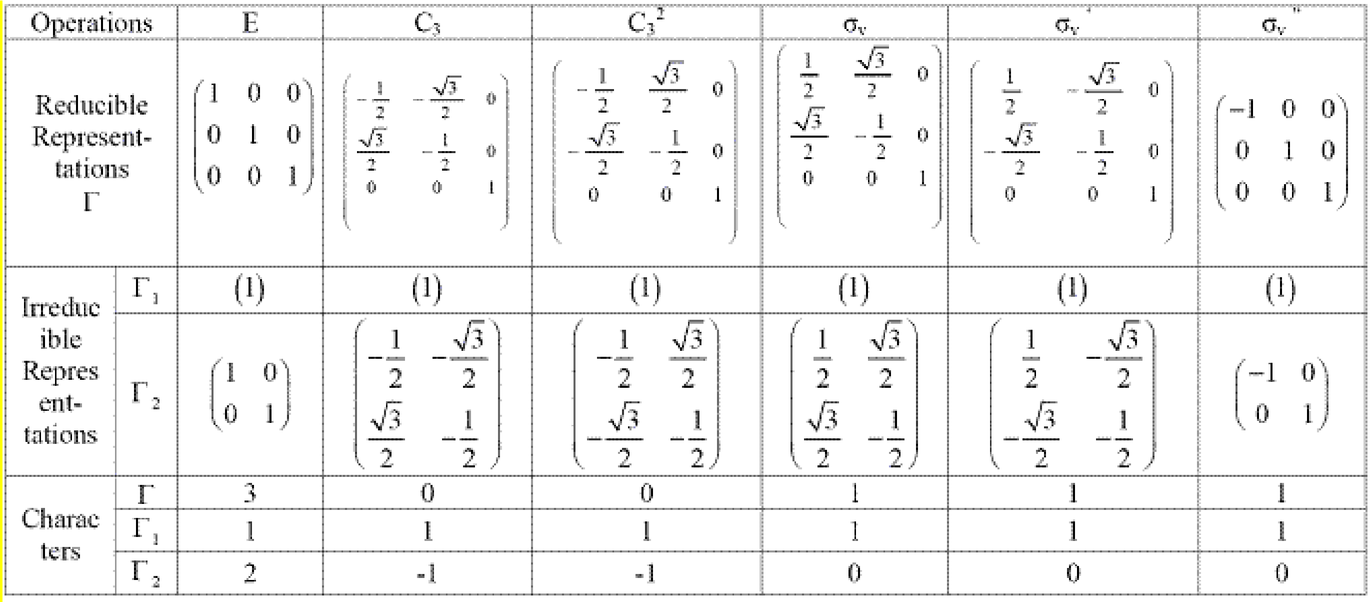
Representations of a Group

Through similarity of transformation, we can define the reducible and irreducible representations of a group. If a matrix representation A can be transferred to block-factored matrix A’, a matrix composed of blocks (A’, A’’, A’’’) at the diagonal and zero in any other position, by similarity transformation, this matrix A is called the reducible representation of this group. And if these blocks (A’, A’’, A’’’) cannot be further transferred to block-factored matrix through similarity transformation, A’, A’’, A’’’ are called irreducible representations of the group. And the sum of the trace of A’, A’’, A’’’ (the number on the diagonal of A’, A’’, A’’’) is called the characters of this representation. As is shown in the following equation, $a_{11}' + a_{22}' + \ldots + a_{nn}'$ is one of the characters. Reducible representations can be reduced to irreducible representations and irreducible representations cannot be reduced further.[1]

$$A' = x^{-1}Ax = x^{-1}\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ a_{n1} & a_{n1} & \ldots & a_{nn} \end{pmatrix} x = \left(\begin{array}{cccccccccccc} a_{11}' & a_{12}' & \cdots & a_{1m}' & & & & & & & & \\ a_{21}' & a_{22}' & \cdots & a_{2m}' & 0 & \cdots & & & & 0 & & \\ \vdots & \vdots & \vdots & \vdots & & & & & & & & \\ a_{m1}' & a_{m1}' & \ldots & a_{mm}' & & & & & & & & \\ & 0 & & & a_{11}'' & a_{12}'' & \cdots & a_{1l}'' & & & & \\ & & & & a_{21}'' & a_{22}'' & \cdots & a_{2l}'' & & & & \\ & \vdots & & & \vdots & \vdots & \vdots & \vdots & & \vdots & & \\ & & & & a_{l1}'' & a_{l1}'' & \ldots & a_{ll}'' & & 0 & & \\ & & & & & & & & a_{11}''' & a_{12}''' & \cdots & a_{1k}''' \\ & 0 & & & 0 & \ldots & & & a_{21}'' & a_{22}'' & \cdots & a_{2k}''' \\ & & & & & & & & \vdots & \vdots & \vdots & \vdots \\ & & & & & & & & a_{k1}''' & a_{k1}''' & \ldots & a_{lk}''' \end{array}\right) = \begin{pmatrix} A' & 0 & 0 \\ 0 & A'' & 0 \\ 0 & 0 & A'' \end{pmatrix}$$

Take C_{3v} as an example.Take (x, y, z) as the basic, the matrix of all the operations in C_{3v} group $\{E, C_3, C_3^2, \sigma_v, \sigma_v', \sigma_v''\}$ are shown in Table 2.6.

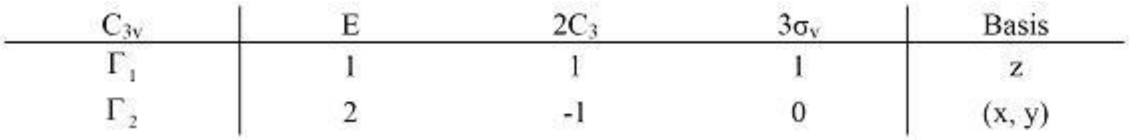
Table 2.6 Reducible and irreducible representations of C_{3v}



Operations		E	C_3	C_3^2	σ_v	σ_v'	σ_v''
Reducible Represent-tations Γ		$\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0\\\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}&\frac{\sqrt{3}}{2}&0\\\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}&-\frac{\sqrt{3}}{2}&0\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}$	$\begin{pmatrix}-1&0&0\\0&1&0\\0&0&1\end{pmatrix}$
Irreducible Represent-tations	Γ_1	(1)	(1)	(1)	(1)	(1)	(1)
	Γ_2	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$	$\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}&\frac{\sqrt{3}}{2}\\\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$	$\begin{pmatrix}\frac{1}{2}&-\frac{\sqrt{3}}{2}\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&1\end{pmatrix}$
Characters	Γ	3	0	0	1	1	1
	Γ_1	1	1	1	1	1	1
	Γ_2	2	-1	-1	0	0	0

As shown in the table 2.6, all the matrix are block-factored matrix and they are reducible representations. Every block in these reducible representations are irreducible representations and the sums of the trace are the characters which are also listed in the table. Notice that the operations in the same class have the same character. Therefore, they are always written together using the new notations $\{E, 2C_3, 3\sigma_v\}$:

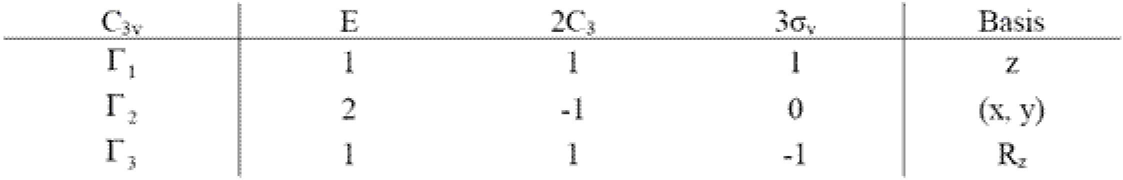
Table 2.7 Two irreducible representations of C_{3v}



C_{3v}	E	$2C_3$	$3\sigma_v$	Basis
Γ_1	1	1	1	z
Γ_2	2	-1	0	(x, y)

This is not a completed table of irreducible representations, because the basis chosen are not completed. There are different kinds of basis, including one-dimensional basis like x, y, z, R_x, R_y, R_z and two-dimensional basis like x_2, y^2, z^2, xy, yz, xz. If we chose R_z which is the rotation around z-axis as another basis, we can get another irreducible representation, (1, 1, -1). “1” means nothing change when operation is applied to the basis. “-1” means it becomes opposite when operation is applied to the basis. “0” means the basis are moved when operation is applied. Therefore, in summary, for now the irreducible representations of C_{3v} group is

Table 2.8 Summary of irreducible representations of C_{3v}



C_{3v}	E	$2C_3$	$3\sigma_v$	Basis
Γ_1	1	1	1	z
Γ_2	2	-1	0	(x, y)
Γ_3	1	1	-1	R_z

Five rules of Characters

For irreducible representations and their characters, there are five very important rules[1]:

Rule 1

The order of the irreducible representation matrix is called the dimension of the irreducible representation, using symbol l_1, l_2, ... And rule 1 states that the sum of the squares of all the dimensions of irreducible representations ($l_1^2+ l_2^2+ \ldots$) is equal to the order of the group, h.

$$?l_i^2=l_1^2+ l_2^2+ \ldots=h$$

Since the character of the irreducible representation of operation E, $?_i(E)$, is equal to the dimension of the corresponding irreducible representation, Rule 1 can also be written as

$$?\ \Gamma_i(E)^2= \Gamma_1(E)^2+ \Gamma_2(E)^2+ \ldots=h$$

Rule 2

Rule 2 is that the sum of the square of the characters in any irreducible representation is equal to h. For example, for the first irreducible representation in C_{3v} group

$$\Gamma_1(E)^2+\Gamma_1(C_3)^2+\Gamma_1(C_3^2)^2+\Gamma_1(\sigma_v)^2+\Gamma_1(\sigma_v{}')^2+\Gamma_1(\sigma_v{}'')^2=1^2+1^2+1^2+1^2+1^2+1^2=6$$

Since for the same class, the characters are the same, it can also be written as

$$\Gamma_1(E)^2+2*\Gamma_1(C_3)^2+3*\Gamma_1(\sigma_v)^2=1^2+2*1^2+3*1^2=6$$

Also, for another irreducible representation in C_{3v} group

$$\Gamma_1(E)^2+2*\Gamma_1(C_3)^2+3*\Gamma_1(\sigma_v)^2=2^2+2*(-1)^2+3*0^2=6$$

Rule 3

Rule 3 is that the vectors which composed of the characters from different irreducible representations are orthogonal.

$$? ?_i(R)^2\Gamma_j(R)^2 = 0 \text{ (i is not equal to j)}$$

Again, take C_{3v} group for an example

$$? \Gamma_1(R)^2\Gamma_2(R)^2 = 1*2+2*1*(-1)+3*1*0=0$$

Rule 4

Rule 4 is that the characters of matrix representations, either reducible or irreducible, of the operations in the same class are the same, which is shown as the former table.

Rule 5

Rule 5 is that the number of irreducible representations **is equal** to the number of classes.

For C_{3v} group, there are three classes and therefore there are also three irreducible representations. Therefore, the three irreducible representations in Table 2.8 are the complete list of irreducible representations in C_{3v} group.

There is a very important relationship between reducible representations and irreducible representations, which is that any reducible representation can be written as the linear combination of irreducible representations. The similarity transformations do not change the character of a reducible representation, therefore

$$\chi(R)=\sum_{j} a_j \chi_j(R)$$

where (R) is the character of reducible representation of operation R. . $_j$(R) is the character of jth irreducible representation. a_j is the times ?$_j$(R) will appear in blocks when reducible representation is reduced to irreducible representation by similarity transformation. To determine a_j, the former equation can be written as

$$\sum_{R} \chi(R)\chi_i(R)=\sum_{R}\sum_{j} a_j \chi_j(R)\chi_i(R)=\sum_{j}\sum_{R} a_j \chi_j(R)\chi_i(R)$$

According to rule 3, only when i=j, the sum over R is not equal to zero. Then according to rule 1, the equation can be written as

$$\sum_{R} \chi(R)\chi_i(R)=ha_i$$

Then rearrange to

$$a_i=\frac{1}{h}\sum_{R} \chi(R)\chi_i(R)$$

Using this equation, we can express reducible representations with irreducible representations, which is very important when we solve chemistry problems.

Again, take C_{3v} group for an example, the reducible representation shown in table 2.6 can be express as combination of irreducible representations using this relationship. Use irreducible representations in table 2.8

a_1= 1/6 [1(3)(1)+2(0)(1)+3(1)(1)] = 1

a_1= 1/6 [1(3)(2)+2(0)(-1)+3(1)(0)] = 1

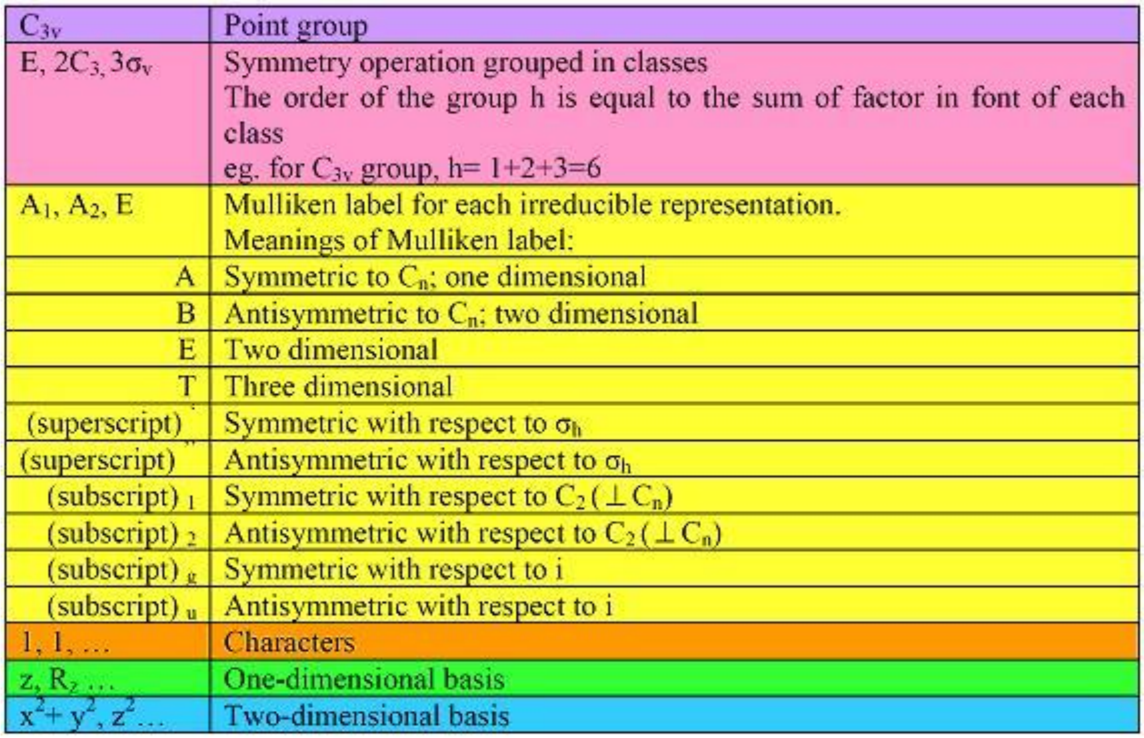
a_1= 1/6 [1(3)(1)+2(0)(1)+3(1)(-1)] = 0

Therefore,

$$\Gamma = 1*\Gamma_1 + 1*\Gamma_2 + 0*\Gamma_3 = \Gamma_1 + \Gamma_2$$

5

Table 2.11 Meanings of different area of character tables



C_{3v}	Point group
E, $2C_3$, $3\sigma_v$	Symmetry operation grouped in classes The order of the group h is equal to the sum of factor in font of each class eg. for C_{3v} group, h= 1+2+3=6
A_1, A_2, E	Mulliken label for each irreducible representation. Meanings of Mulliken label:
A	Symmetric to C_n; one dimensional
B	Antisymmetric to C_n; two dimensional
E	Two dimensional
T	Three dimensional
(superscript) '	Symmetric with respect to σ_h
(superscript) ''	Antisymmetric with respect to σ_h
(subscript) $_1$	Symmetric with respect to C_2 ($\perp C_n$)
(subscript) $_2$	Antisymmetric with respect to C_2 ($\perp C_n$)
(subscript) $_g$	Symmetric with respect to i
(subscript) $_u$	Antisymmetric with respect to i
1, 1, …	Characters
z, R_z …	One-dimensional basis
x^2+y^2, z^2…	Two-dimensional basis

Using this flow chart, you can determine the symmetries of small molecules. And also, by using group theory and character tables, you can determine the symmetries of any thing you are interested in, such as molecular orbitals, vibrational modes, etc. In conclusion, group theory play a very important role in chemistry, which we can see from various applications of group theory in chemistry, like Infrared spectrum, Raman spectrum, electronic spectrum, etc.

Matrix Representations of Groups

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 $\Gamma(g)$(g), one for each symmetry element gg. 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.

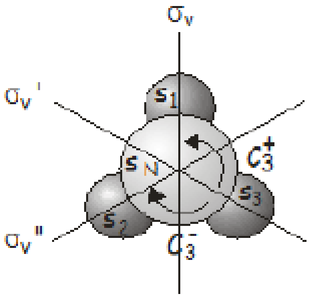
1. The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.
2. The 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 C_{3v}point group, we showed that the combined symmetry operation $C_3\sigma_v$ is equivalent to σ''_v. In a matrix representation of the group, if the matrix representatives of C_3 and σ_v are multiplied together, the result will be the representative of σ''_v.

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.

Example: a matrix representation of the C_{3v} point group (the ammonia molecule)

The first thing we need to do before we can construct a matrix representation is to choose a basis. For NH_3, we will select a basis (s_N, s_1, s_2, s_3) 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 C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarized in the figure below.



The effects of the symmetry operations on our chosen basis are as follows:

$$E\ (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3)$$

$$C^{+3}(s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1)$$

$$C^{-3}(s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2)$$

$$\sigma_v\ (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2)$$

$$\sigma'_v\ (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3)$$

$$\sigma''_v\ (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \qquad (10.1)$$

By inspection, the matrices that carry out the same transformations are:

$$\Gamma\ E\ (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3)$$

$$\Gamma\ C^{+3}(s_N,s_1,s_2,s_3)\rightarrow(s_N,s_2,s_3,s_1)$$

$$\Gamma\ C^{-3}(s_N,s_1,s_2,s_3)\rightarrow(s_N,s_3,s_1,s_2)$$

$$\Gamma\ \sigma_v\ (s_N,s_1,s_2,s_3)\rightarrow(s_N,s_1,s_3,s_2)$$

$$\Gamma\ \sigma'_v\ (s_N,s_1,s_2,s_3)\rightarrow(s_N,s_2,s_1,s_3)$$

$$\Gamma\ \sigma''_v\ (s_N,s_1,s_2,s_3)\rightarrow(s_N,s_3,s_2,s_1)$$

These six matrices therefore form a representation for the C_{3v} point group in the (s_N,s_1,s_2,s_3) basis. They multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

SUGGESTED READINGS

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.

Possible Questions

PART- A Questions (Each question carry 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 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 ofthe
   a. **angular momentum operator** b. Lapalacian 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. 1σg c. **1a1** d. C_3v

10. The benzene molecule C6H6 has how many
   vibrational modes a. 6 b. 12 c.
   24d. **30**

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. En=2n-1/2 b. $En=n^2$ c. **En is continuous** d. $En \alpha n^2$

13. The shape of BeCl2 molecules is
   a. **Linear** b. Triangular planar c. Tetrahedral d. octahedral

KAHE

14. Example for tetrahedral molecule
    a. BeCl2 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
    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 theoryin explaining the results of black body radiation experiment.

(OR)

(b). Write notes on photoelectric effect.

KAHE

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)

(iv) (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)

1. Discuss about Reducible and Irreducible representations.
2. Construct the character table for C_{3v} point group.

KAHE

KAHE

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
I M.SC CHEMISTRY (2019-2021 BATCH)
SUBJECT: PHYSICAL CHEMISTRY-I (QUANTUM CHEMISTRY AND GROUP THEORY)
SUBJECT CODE: 19CHP103
MULTIPLE CHOICE QUESTIONS(EACH QUESTION CARRY ONE MARK)
UNIT -4

S. NO	**Question**	**Option A**	**Option B**	**Option C**	**Option D**	**Answer**
1	The sha+A187+A188:B188+A188:C188+A18+A188:C189	Linear	Triangular planar	Tetrahedral	octahedral	Linear
2	The shape of boron trifluoride is	Linear	Triangular planar	Tetrahedral	octahedral	Triangular planar
3	The structure of methane is	Linear	Triangular planar	Tetrahedral	octahedral	tetrahedral
4	Structure of phosphorous pentachloride is	Linear	Trigonal bipyramidal	Tetrahedral	octahedral	Trigonal bipyramidal

KAHE

KAHE

5	Example for a linear molecule	$BeCl_2$	boron trifluoride	methane	phosphorous pentachloride	$BeCl_2$
6	Example for triangular planar molecule	$BeCl_2$	boron trifluoride	methane	phosphorous pentachloride	boron trifluoride
7	Example for tetrahedral molecule	$BeCl_2$	boron trifluoride	methane	phosphorous pentachloride	methane
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

KAHE

KAHE

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

KAHE

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

KAHE

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

KAHE

KAHE

28	The molecule which possess two planes of symmetry is	$BeCl_2$	water	Boron trifluoride	Phosphorous pentachloride	water
29	The molecule which possesses Cα 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

KAHE

KAHE

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 $D_{\alpha h}$ 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	$D_{\alpha h}$
45	The point group of acetylene is	$D_{\alpha h}$	C_{2v}	C_{3v}	D_{3h}	C_{2v}
46	The point group of water is	$D_{\alpha h}$	C_{2v}	C_{3v}	D_{3h}	C_{3v}
47	The point group of ammonia is	$D_{\alpha h}$	C_{2v}	C_{3v}	D_{3h}	D_{3h}
48	The point group of boron trichloride is	$D_{\alpha h}$	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

KAHE

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 coordination 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

KAHE

KAHE

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

KAHE

LECTURE NOTES

UNIT-5(Group theory)

SYLLABUS

UNIT-5 GROUP THEORY

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.

Irreducible Representation

An irreducible representation of a group is a group representation that has no nontrivial invariant subspaces. For example, the orthogonal group $O(n)$ has an irreducible representation on $\mathbb{R}^n$.

Any representation of a finite or semisimple Lie group breaks up into a direct sum of irreducible representations. But in general, this is not the case, e.g., $(\mathbb{R}, +)$ has a representation on $\mathbb{R}^2$ by

$$\phi(a) = \begin{bmatrix} 1 & a \\ 0 & 1 \end{bmatrix}, \qquad (1)$$

i.e., $\phi(a)(x, y) = (x + a\,y, y)$. But the subspace $y = 0$ is fixed, hence ϕ is not irreducible, but there is no complementary invariant subspace.

The irreducible representation has a number of remarkable properties, as formalized in the group orthogonality theorem. Let the group order of a group be h, and the dimension of the ith representation (the order of each constituent matrix) be l_i (a positive integer). Let any operation be denoted R, and let the mth row and nth column of the matrix corresponding to a matrix R in the ith irreducible representation be $\Gamma_i(R)_{mn}$. The following properties can be derived from the group orthogonality theorem,

$$\sum_R \Gamma_i (R)_{mn}\, \Gamma_j (R)_{m'n'}{}^* = \frac{h}{\sqrt{l_i\, l_j}}\, \delta_{ij}\, \delta_{mm'}\, \delta_{nn'}. \tag{2}$$

1. The dimensionality theorem:

$$h = \sum_i l_i^2 = l_1^2 + l_2^2 + l_3^2 + \ldots = \sum_i \chi_i^2 (I), \tag{3}$$

where each l_i must be a positive integer and χ is the group character (trace) of the representation.

2. The sum of the squares of the group characters in any irreducible representation i equals h,

$$h = \sum_R \chi_i^2 (R). \tag{4}$$

3. Orthogonality of different representations

$$\sum_R \chi_i (R)\, \chi_j (R) = 0 \text{ for } i \neq j. \tag{5}$$

4. In a given representation, reducible or irreducible, the group characters of all matrices belonging to operations in the same class are identical (but differ from those in other representations).

5. The number of irreducible representations of a group is equal to the number of conjugacy classes in the group. This number is the dimension of the Γmatrix (although some may have zero elements).

6. A one-dimensional representation with all 1s (totally symmetric) will always exist for any group.

7. A one-dimensional representation for a group with elements expressed as matrices can be found by taking the group characters of the matrices.

8. The number a_i of irreducible representations χ_i present in a reducible representation c is given by

$$a_i = \frac{1}{h} \sum_R \chi (R)\, \chi_i (R), \tag{6}$$

where h is the group order of the group and the sum must be taken over all elements in each class. Written explicitly,

$$a_i = \frac{1}{h} \sum_R \chi (R)\, \chi_i{}' (R)\, n_R, \tag{7}$$

where χ_i' is the group character of a single entry in the character table and n_R is the number of elements in the corresponding conjugacy class.

Irreducible representations can be indicated using Mulliken symbols.

Direct Products of Irreducible Representations

Every molecule has a point group associated with it, which are assigned by a set for rules (explained by Group theory). The character tables takes the point group and represents all of the symmetry that the molecule has.

Symbols under the first column of the character tables

A (Mulliken Symbol)	(singly degenerate or one dimensional) symmetric with respect to rotation of the principle axis
B (Mulliken Symbol)	(singly degenerate or one dimensional) anti-symmetric with respect to rotation of the principle axis
E (Mulliken Symbol)	(doubly degenerate or two dimensional)
T (Mulliken Symbol)	(thirdly degenerate or three dimensional)
Subscript 1	symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_v
Subscript 2	anti-symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_v
Subscript g	symmetric with respect to the inverse
subscript u	anti-symmetric with respect to the inverse

prime	symmetric with respect to $\sigma h\sigma h$ (reflection in horizontal plane)
double prime	anti-symmetric with respect to $\sigma h\sigma h$ (opposite reflection in horizontal plane)

Symbols in the first row of the character tables

E	describes the degeneracy of the row (A and B= 1) (E=2) (T=3)
C_n	2pi/n= number of turns in one circle on the main axis without changing the look of a molecule (rotation of the molecule)
C_n'	$2\pi/n$= number of turns in one circle perpendicular to the main axis, without changing the structure of the molecule
C_n''	$2\pi/n$= number of turns in one circle perpendicular to the C_n' and the main axis, without changing the structure
σ'	reflection of the molecule perpendicular to the other sigma
σ_v (vertical)	reflection of the molecule vertically compared to the horizontal highest fold axis.
σ_h or $_d$ (horizontal)	reflection of the molecule horizontally compared to the horizontal highest fold axis.

i	Inversion of the molecule from the center
S_n	rotation of 2π/n and then reflected in a plane perpendicular to rotation axis.
#C_n	the # stands for the number of irreducible representation for the C_n
#σ	the # stands for the number irreducible representations for the sigmas.
the number in superscript	in the same rotation there is another rotation, for instance O_h has $3C_2=C_4^2$
other useful definitions	
(R_x,R_y)	the (,) means they are the same and can be counted once.
x^2+y^2, z^2	without (,) means they are different and can be counted twice.

Looking at a Character Table

D_3h	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	IR	Raman

A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
$A_{2''}$	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xy, yz)

The order is the number in front of the the classes. If there is not number then it is considered to be one. The number of classes is the representation of symmetries.The D_3h has six classes and an order of twelve.

Understanding using matrix

The identity does nothing to the matrix.

[1 0 0] [X] [X]

[0 1 0] [Y] = [Y]

[0 0 1] [Z] [Z]

$\sigma_{(xy)}$ the x and y stay positive, while z turns into a negative.

[1 0 0] [X] [X]

[0 1 0] [Y] = [Y]

[0 0 -1] [Z] [-Z]

Inversion (I) is when all of the matrix turns into a negative.

[-1 0 0] [X] [-X]

[0 -1 0] [Y] = [-Y]

[0 0 -1] [Z] [-Z]

$C_n$is when one would use cos and sin. for an example C_4

[cos (2π/4 -sin (2π/4 0] [X] []

[sin (2π/4) cos (2π/4) 0] [Y] = []

[0 0 1] [Z] []

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)

Ti = ith representation

li = dimension of Ti (e.g. 3 × 3 , li = 3)

R = generic symbol for an operator

[Ti R(mn)] = the element in the mth row and nth column of an operator R in representation Ti[Tj R(m’n’)] = complex conjugate of the elementin the m’th row and n’th column of an operator R in representation Tj. What does this all mean?

For any two irreducible representations Ti, Tj

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/li

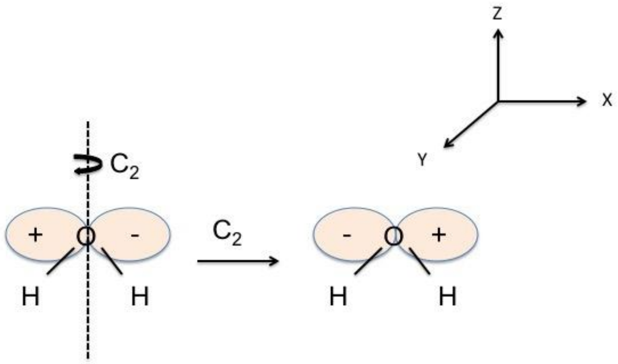
Character Tables

Once the point group of a molecule is known, we can begin to make use of character tables. Group theoretical considerations and matrix algebra have produced a solid mathematical foundation for the information found in character tables. However, it would be too lengthy and beyond the scope of this course to cover this material rigorously. Fortunately, it is not necessary to have a full and complete understanding of the background theory in order to be able to use character tables to solve problems related to symmetry. We will approach the material from a more descriptive view point.

What is a Character Table?

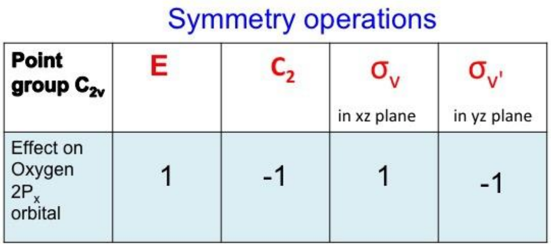
As we shall shortly discover, each point group has its own unique character table which is a device containing useful symmetry related information. A simple way of thinking about how a character table is constructed is to firstly, recognize that the positions of the atoms of a molecule (let's say water for example) conform exactly and precisely to the symmetry operations for the point group to which it belongs (C_{2v} for example). That is, the appearances of the molecule before and after a symmetry operation are identical. However, molecules have other important properties which do not behave in exactly the same way as the positions of the atoms. These properties are often referred to as molecular properties, and can include simple translations, rotations, vibrations, and even the behavior of electrons in atomic orbitals. They are also referred to as "basis vectors."

An example of how we might generate information relating to a particular molecular property is to first agree to characterize symmetric behavior at +1 and antisymmetric behavior as -1, and to call the +1's and -1's the *character* of the property with respect to the symmetry operation. For water, we place the O atom at the origin of the cartesian coordinate system and examine the behavior of the P_x orbital on O. [Note that the + and - in the figure refer to the angular dependence of the wave function.]
We now perform one of the symmetry operations for C_{2v} (ignore the positions of the O and H atoms for the moment). If we choose the C_2 operation then we would rotate the molecule about the Z axis.



Effect on oxygen $2P_x$ orbital when C_2 operation is performed.

The sign of the wave function changes and we describe this as antisymmetric behavior and give it the character -1. We can perform this analysis for all four operations for C_{2v} and tabulate the results.

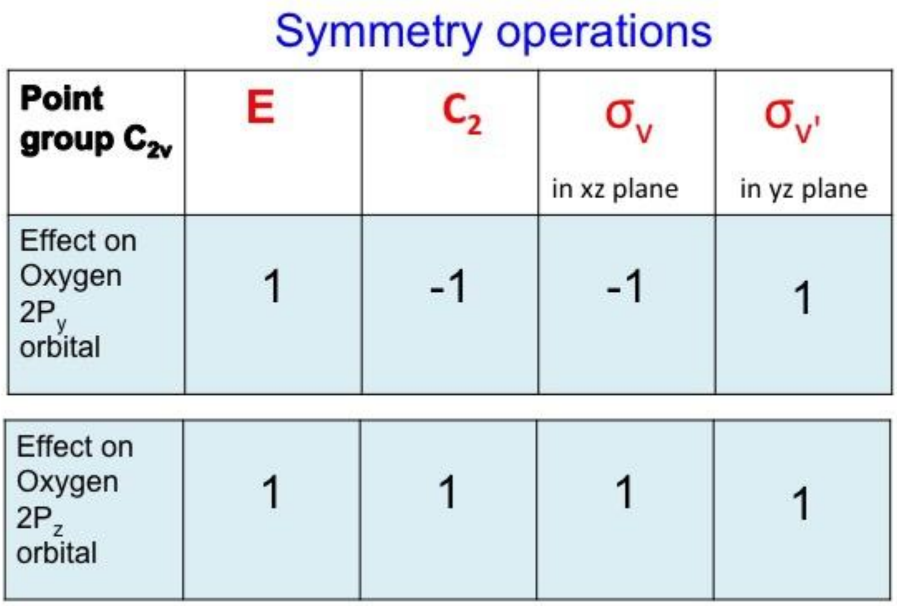


Symmetry operations

Point group C_{2v}	E	C_2	σ_v in xz plane	$\sigma_{v'}$ in yz plane
Effect on Oxygen $2P_x$ orbital	1	-1	1	-1

1 = unaffected or unchanged
-1 = changed or reversed

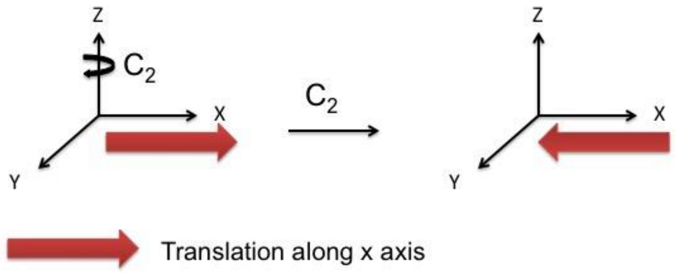
A similar treatment for the oxygen P_y and P_z orbitals gives the following table



Symmetry operations

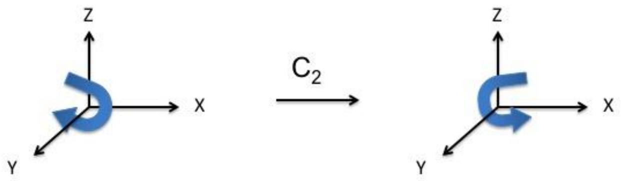
Point group C_{2v}	E	C_2	σ_v in xz plane	$\sigma_{v'}$ in yz plane
Effect on Oxygen $2P_y$ orbital	1	-1	-1	1
Effect on Oxygen $2P_z$ orbital	1	1	1	1

At this point we should also point out that the P orbitals lie along the x, y, and z axes, and the information that we have generated in the tables can equally be used to describe *translations* of the molecule. A translation is the movement of a molecule as a whole. T_x stands for translation along the x axis, and this can be depicted as an arrow pointing along the x direction. Performing the C_2 operation reverses the direction of the arrow and so we assign this a -1 character (just like a P_x orbital). Since we live in a 3-dimensional universe, there are three translations T_x, T_y, and T_z representing three degrees of freedom for the molecule.



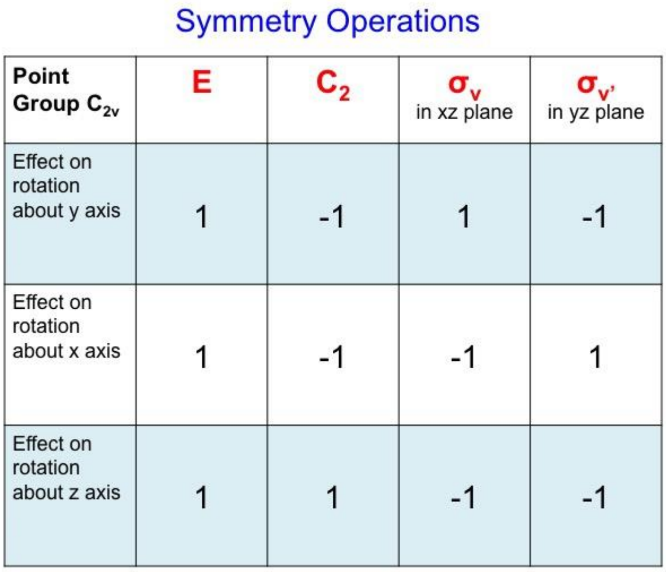
Effect on translation along the x axis when C_2 operation is performed

In much the same way as we treated P orbitals and translations (by "inspection") we can also consider rotations of the molecule as a whole. Again, there are three possible rotations R_x, R_y, and R_z which can be performed by rotations about the x, y, and z axes respectively. Consider the rotation R_y as if it were the steering wheel of an automobile - depicted here with a curly arrow. After the C_2 operation, the direction of turn of the automobile has been reversed (clockwise to anticlockwise) and so we assign a -1 character.



Effect on rotation about y axis (R_y) when C_2 operation is performed

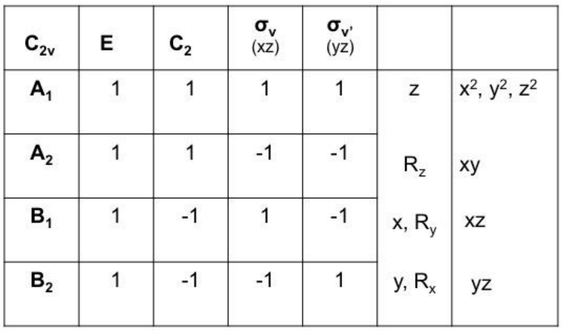
For R_y, a table of the effect on rotation about the y axis looks like this (rotations about the x and y axis have also been added)



Symmetry Operations

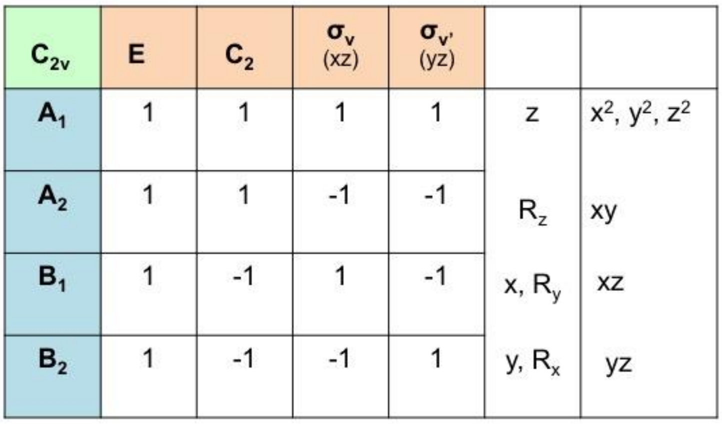
Point Group C_{2v}	E	C_2	σ_v in xz plane	$\sigma_{v'}$ in yz plane
Effect on rotation about y axis	1	-1	1	-1
Effect on rotation about x axis	1	-1	-1	1
Effect on rotation about z axis	1	1	-1	-1

We can condense this information about the molecular properties of water into a table - a Character Table. The character table for water (C_{2v}) is shown below

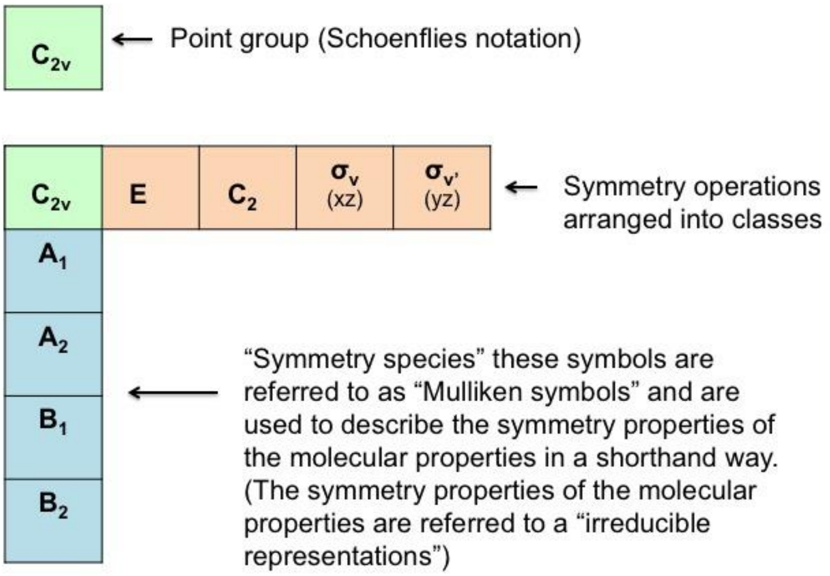


C_{2v}	E	C_2	σ_v (xz)	$\sigma_{v'}$ (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The various parts of the table can be described as follows [Note that some of this nomenclature comes from the mathematical underpinning of group theory - don't be put off by it!]



C_{2v}	E	C_2	σ_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



← Point group (Schoenflies notation)

← Symmetry operations arranged into classes

"Symmetry species" these symbols are referred to as "Mulliken symbols" and are used to describe the symmetry properties of the molecular properties in a shorthand way. (The symmetry properties of the molecular properties are referred to a "irreducible representations")

C_{2v}	E	C_2	σ_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

↑

The molecular properties (translations, rotations) assigned to their symmetry species. Also called "the basis functions" of the irreducible representations. You will always find 6 symbols here (x, y, z, R_x, R_y, R_z). They represent mathematical functions such as orbitals, rotations etc.

$\mathbf{C_{2v}}$	**E**	$\mathbf{C_2}$	$\boldsymbol{\sigma_v}$ (xz)	$\boldsymbol{\sigma_{v'}}$ (yz)		
$\mathbf{A_1}$	1	1	1	1	z	x^2, y^2, z^2
$\mathbf{A_2}$	1	1	-1	-1	R_z	xy
$\mathbf{B_1}$	1	-1	1	-1	x, R_y	xz
$\mathbf{B_2}$	1	-1	-1	1	y, R_x	yz

A "representation" of the symmetry properties of certain molecular properties – this line is a representation of how translations in the x-direction (x) and rotations about the y axis (Ry) behave in C_{2v} point group symmetry. This is actually a mathematical code, and is found here in its simplest form - it is therefore referred to as an ***"irreducible representation"*** (Can also be referred to as "symmetry species").

$\mathbf{C_{2v}}$	**E**	$\mathbf{C_2}$	$\boldsymbol{\sigma_v}$ (xz)	$\boldsymbol{\sigma_{v'}}$ (yz)		
$\mathbf{A_1}$	1	1	1	1	z	x^2, y^2, z^2
$\mathbf{A_2}$	1	1	-1	-1	R_z	xy
$\mathbf{B_1}$	1	-1	1	-1	x, R_y	xz
$\mathbf{B_2}$	1	-1	-1	1	y, R_x	yz

The "character" of an irreducible representation (symbol χ chi).

What do Mulliken Symbols Stand For?


Robert S. Mulliken

Mulliken symbols were proposed by Robert S. Mulliken (1896-1986, Nobel prize in chemistry 1966) and are intended to have the following meanings:

A or B stand for one dimensional representations

A - is symmetric with respect to rotation about a principal axis (C_n)

B- is antisymmetric with respect to rotation about a principal axis (C_n)

E - stands for a doubly degenerate representation

T - stands for a three dimensional representation

Subscripts 1 and 2 refer to symmetry with respect to a C_2 axis perpendicular to a principle axis (C_n), or to a vertical plane of symmetry if there is no C_2

1- symmetric

2 - antisymmetric

Primes (') or ('') stand for symmetric (') or antisymmetric ('') with respect to a horizontal plane of symmetry (σ_h)

In point groups which have a center of symmetry (i) the subscripts g and u stand for g - symmetric

u - antisymmetric

with respect to inversion.

A Few Last Comments about Character Tables

In this course you will **NOT** have to:

1. Determine the characters of an irreducible representation

2. Generate or create a character table or memorize any

3. Perform complex math using character tables

Normal Modes of Vibration

What use are character tables?

At this point a good question is: what's the point of learning about character tables? The simple answer is that the symmetry and associated character table of a molecule can be used to interpret and predict many aspects of chemically significant spectroscopies as well as bonding. We will illustrate this next by focussing on the vibrational modes of a molecule.

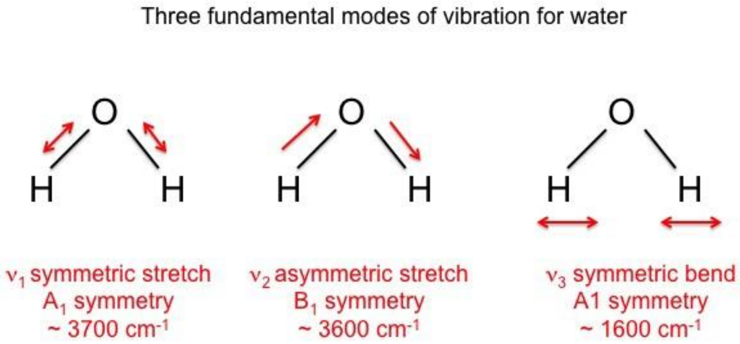
In the laboratory we can gather useful experimental data using infra-red (IR) and Raman spectroscopy. This data can be compared to the number of IR and/or Raman active bands predicted from the application of group theory and the correct character table. The mathematics (group theory and matrix algebra) behind this treatment serves as a solid theoretical foundation. The manipulations described below work because all the symmetry operations of a molecule comprise a mathematical group and obey the rules of the group. As noted previously we do not have to master this area of mathematics in order to make good use of character tables.

Degrees of Freedom and Vibrations in Molecules

Here we will initially discuss the degrees of freedom for a simple molecule (water). We will very quickly see why it is very beneficial to employ symmetry when investigating larger molecules.

For a molecule with "N" atoms there are 3N degrees of freedom (remember we live in a 3-dimensional world of x, y, z coordinates). For a non-linear molecule 3 degrees of freedom can be signed to translations - movement of a body as a whole (T_x, T_y, T_z) and 3 to rotations (R_x, R_y, R_z). The remaining motions of the atoms are displacements of the atoms from their mean positions - the center of gravity does not change. These fundamental vibrations are referred to as "normal modes". Thus, a non-linear molecule has 3N-6 normal modes. For water the number of normal modes is 3 (3 x 3 - 6 = 3). For linear molecules there are 3N-5 normal modes.

For water, which of course has been intensively studied we know that the 3 vibrations are as follows.

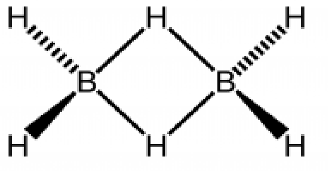


The symbols used to describe these modes (A_1, B_1) are the same Mulliken symbols that we encountered in our discussion of character tables. In other words, the vibrations, which are molecular properties, can described by symmetry species or irreducible representations. In fact much of the literature involving vibrational spectroscopy uses these symbols as a shorthand way of communicating information.

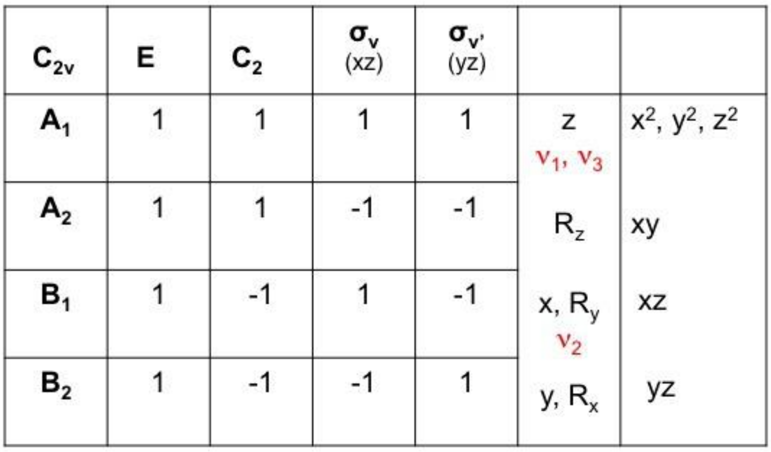
It should be pretty obvious that the number of vibrations increases rapidly with even modest increases in the number of atoms in the molecule. Determining the kinds of vibrations by inspection (as we did for water) now becomes much more difficult. For example consider the following compounds:

H_2O	3 atoms	3 vibrations
PH_3	4 atoms	6 vibrations
CO_2^{2-}	4 atoms	6 vibrations
XeF_4	5 atoms	9 vibrations
B_2H_6	8 atoms	18 vibrations

For diborane (B_2H_6) which has D_{2h} symmetry figuring out the nature and symmetry species of all 18 vibrations by inspection would be a daunting task. However, armed with the character table for D_{2h} and knowledge of symmetry properties the task of determining the symmetry species of all vibrations is straight-forward.

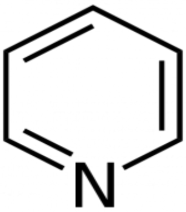


For the case of water we could present the character table (C_{2v}) with the 3 vibrations (v1, v2, v3) listed in the column of molecular properties as shown below. (ν = Greek symbol "nu")



C_{2v}	E	C_2	σ_v (xz)	$\sigma_{v'}$ (yz)		
A_1	1	1	1	1	z ν_1, ν_3	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y ν_2	xz
B_2	1	-1	-1	1	y, R_x	yz

However, in general this approach is impractical. Take pyridine (C_5H_5N) for example. The point group is also C_{2v} but the molecule has 11 atoms. The number of fundamental modes of vibration is 27 (3 x 11 - 6 = 27).



In this case we would have to draw up a C_{2v} character table showing the symmetries of all 27 vibrations. For this reason vibrations are not normally included in character tables. Instead it is up to the user (you) to determine the number and type of vibrations (as defined by their symmetry species) for any molecules that are encountered. How we do this is described below.

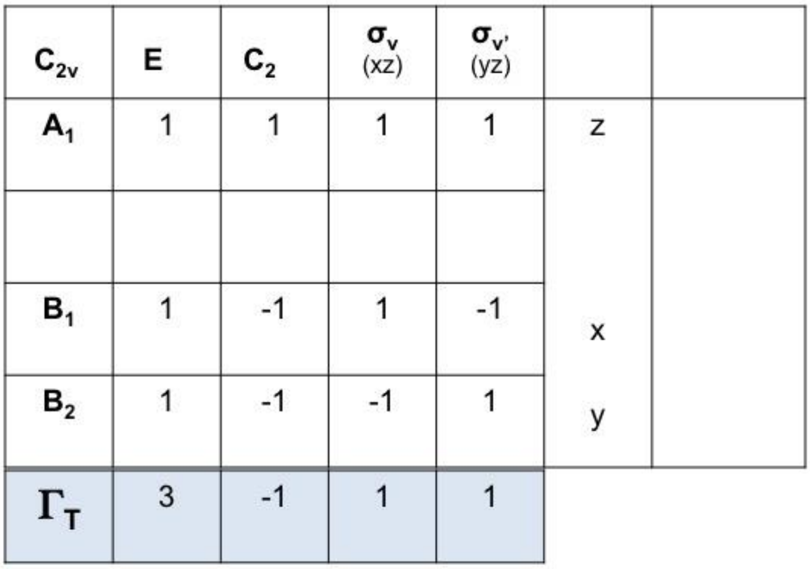
Reducible Representations

As previously noted one of the important properties of character tables is that the symmetry operations are members of a mathematical group and important relationships exist between them. In general the same can be said about the symmetry species or irreducible representations of the molecular properties. The products from combining the characters of irreducible representations either by multiplication or addition/subtraction also obey the rules of the group. The new representations are no longer the most simple possible and are referred to as "reducible representations" because they can be "reduced" down to their component parts.

For example, for water the symmetries of the translations (T_x, T_y, T_z) can be gleaned directly from the C_{2v} character table. They are A_1, B_1, and B_2. We can represent all three of these degrees of freedom by a representation $\mathbf{\Gamma_T}$ and we can write the expression below. ($\mathbf{\Gamma}$ = upper case Greek letter "gamma").

$\mathbf{\Gamma_T} = A_1 + B_1 + B_2$

We know that A_1, B_1 and B_2 are merely the shorthand notations for the symmetry species (irreducible representations). We can therefore simply write down the characters of $\mathbf{\Gamma_T}$ by adding the individual characters for A_1, B_1 and B_2 from the C_{2v} character table.

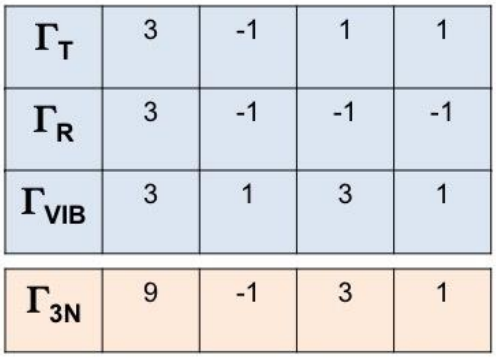


C_{2v}	E	C_2	σ_v (xz)	$\sigma_{v'}$ (yz)		
A_1	1	1	1	1	z	
B_1	1	-1	1	-1	x	
B_2	1	-1	-1	1	y	
Γ_T	3	-1	1	1		

Thus $\mathbf{\Gamma_T}$ = 3 -1 1 1.

This is a valid reducible representation and a member of the C_{2v} group.

In a similar manner we can write down the reducible representation for all three rotations and all the vibrations.



Γ_T	3	-1	1	1
Γ_R	3	-1	-1	-1
Γ_{VIB}	3	1	3	1
Γ_{3N}	9	-1	3	1

The representation for ALL the degrees of freedom for the molecule (3N) can be written as

$\boldsymbol{\Gamma_{3N} = \Gamma_T + \Gamma_R + \Gamma_{VIB}}$

and the reducible representation for it is obtained by simply summing the characters for $\boldsymbol{\Gamma_T}$**,** $\boldsymbol{\Gamma_R}$ and $\boldsymbol{\Gamma_{VIB}}$**.**

$\boldsymbol{\Gamma_{3N}}$ = 9 -1 3 1

Make a note of this - it will come up later!

Although the set of characters 9 -1 3 1 is a valid member of the C_{2v} group it is not particularly useful when discussing molecular properties. What is really required is the language of the shorthand symmetry species (Mulliken symbols, A_1, B_1 etc.). In other words we want to express $\boldsymbol{\Gamma_{3N}}$ in terms of A_1, B_1 etc. From the information covered above it can be easily shown by inspection that:

$\boldsymbol{\Gamma_{3N}} = 3A_1 + A_2 + 3B_1 + 2B_2$

The good news is that for other more complex molecules we do not have to perform this task by inspection because:

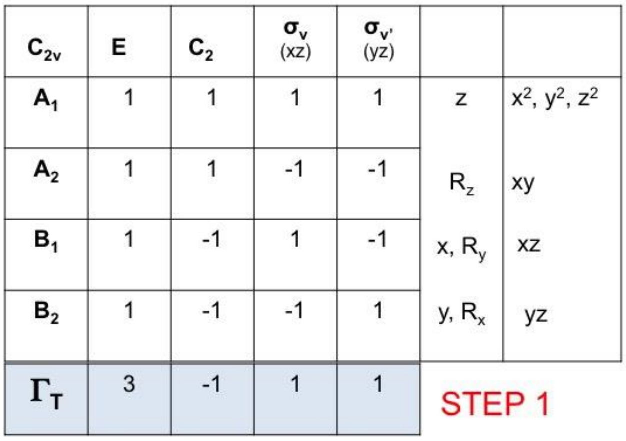
1. We can easily generate $\boldsymbol{\Gamma_{3N}}$ as a reducible representation for a molecule (if we know its point group symmetry).

2. We can easily convert the **Γ_{3N}** reducible representation into the sum of its symmetry species (Mulliken symbols) using a "simple" formula known as the reduction formula.

General Method to Obtain Γ_{3N}

Step 1

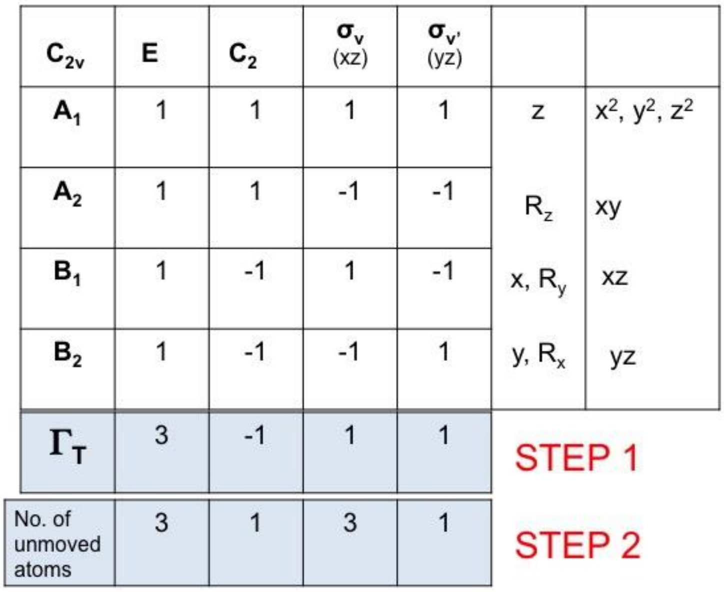
Take the character table for the molecule and add a row at the bottom. In this row generate the reducible representation for **Γ_T** (or **Γ_{xyz}**) as we did above, simply by adding the characters for each operation which correspond to the molecular properties for x, y and z. For C_{2v} we have already shown that these are the characters corresponding to A_1, B_1 and B_2.



C_{2v}	E	C_2	σ_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
Γ_T	3	-1	1	1	STEP 1	

Step 2

Add another row below **Γ_T** and write down the number of atoms which **DO NOT CHANGE**their location during each symmetry operation. This is where you realize how useful a real molecular model set is. To do this you will also need to know where the symmetry elements are and how the symmetry operations affect the molecule. Of course, you already know how to do this because you have studied Schönflies notation and know how to assign the point group of a molecule. The character table also has all the symmetry operations listed by class along the top row.

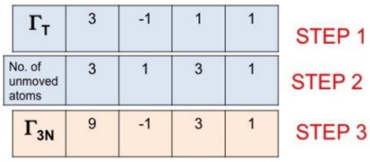


C_{2v}	E	C_2	σ_v (xz)	$\sigma_{v'}$ (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
Γ_T	3	-1	1	1	STEP 1	
No. of unmoved atoms	3	1	3	1	STEP 2	

Thus for water (3 atoms) under E there are 3 unmoved atoms, but for C_2 both H's move but since the O atom sits on the C_2 axis it does not change its location and so we record 1 under the C_2 column. The new set of numbers generated in step 2 (3 1 3 1) is also a reducible representation in C_{2v} and obeys the rules of the group.

Step 3

In this step we simply multiply together the characters that have been generated in steps 1 and 2. The result (third row) is the reducible representation for $\mathbf{\Gamma_{3N}}$ (or $\mathbf{\Gamma_{TOT}}$). Its that simple.

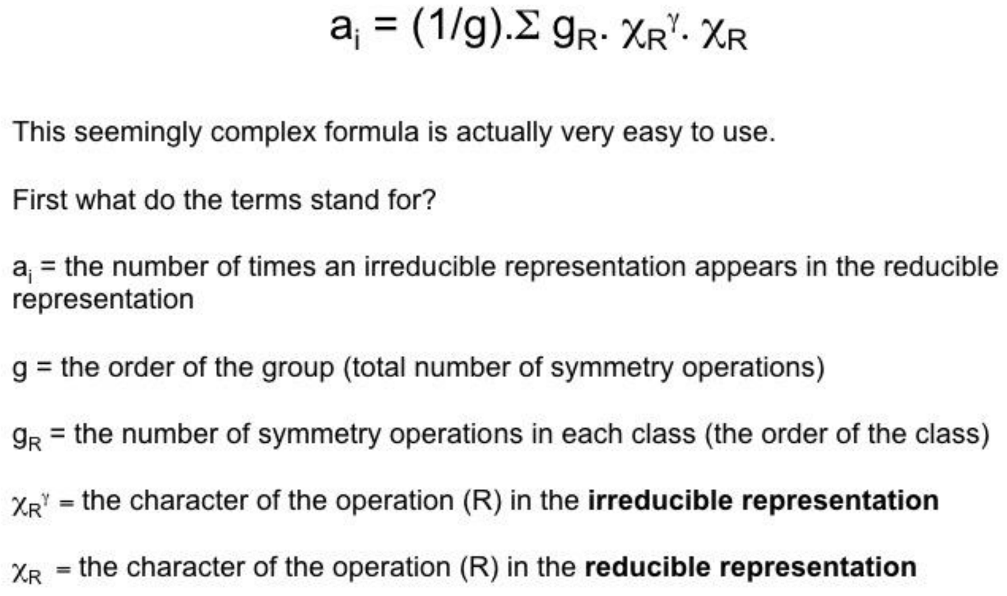


Γ_T	3	-1	1	1	STEP 1
No. of unmoved atoms	3	1	3	1	STEP 2
Γ_{3N}	9	-1	3	1	STEP 3

You will note that the new reducible representation (9 -1 1 3) is identical to the representation for $\mathbf{\Gamma_{3N}}$ that we obtained previously by inspection.

Reducing the Reducible Representation

To convert ANY reducible representation into the sum of its irreducible representations (symmetry species or Mulliken symbols) we use a reduction formula:



$$a_i = (1/g).\Sigma\, g_R \cdot \chi_R^{\gamma} \cdot \chi_R$$

This seemingly complex formula is actually very easy to use.

First what do the terms stand for?

a_i = the number of times an irreducible representation appears in the reducible representation

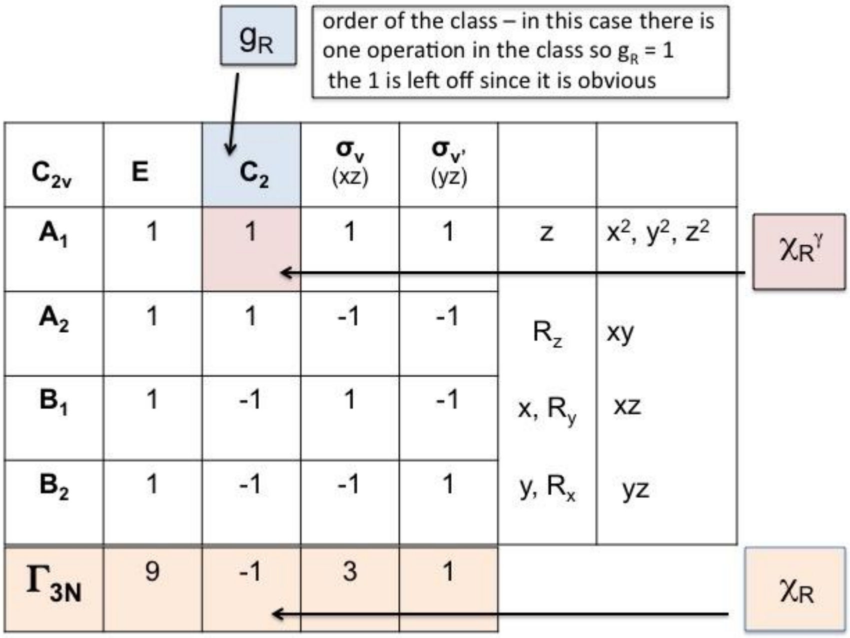
g = the order of the group (total number of symmetry operations)

g_R = the number of symmetry operations in each class (the order of the class)

χ_R^{γ} = the character of the operation (R) in the **irreducible representation**

χ_R = the character of the operation (R) in the **reducible representation**

You can easily find this information in the character table:



order of the class – in this case there is one operation in the class so $g_R = 1$ the 1 is left off since it is obvious

C_{2v}	E	C_2	σ_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
Γ_{3N}	9	-1	3	1		

Back to our example for water: Point group C_{2v}, order (g) = 4

The reducible representation for $\mathbf{\Gamma_{3N}}$ = 9 -1 3 1

The number of times A_1 appears in this representation is therefore

a_{A1} = 1/4 { 1.1.9 + 1.1. (-1) + 1.1.3 +1.1.1} = 3

so $\mathbf{\Gamma_{3N}}$ contains 3 A_1 symmetry species. The numbers of the other symmetry species are calculated as follows:

a_{A2} = 1/4 { 1.1.9 + 1.1.(-1) + 1.(-1).3 + 1.(-1).1 } = 1 one A_2 present

a_{B1} = 1/4 { 1.1.9 + 1.(-1).(-1) + 1.1.3 + 1.(-1).1} = 3 3 B_1 present

a_{B2} = 1/4 {1.1.9 + 1.(-1)(-1) + 1.(-1).3 + 1.1.1} = 2 2 B_2 present

We can now write $\mathbf{\Gamma_{3N}} = 3A_1 + A_2 + 3B_1 + 2B_2$ (exactly what we got by "inspection" above. We can now subtract the symmetry species for the translations and rotations and this will give us the number and symmetry species of the fundamental modes of vibration. $\mathbf{\Gamma_T}$ and $\mathbf{\Gamma_R}$ can be obtained directly from the character table.

$\mathbf{\Gamma_{3N}} = 3A_1 + A_2 + 3B_1 + 2B_2$

$\mathbf{\Gamma_T} = A_1 + B_1 + B_2$

$\mathbf{\Gamma_R} = A_2 + B_1 + B_2$

$\mathbf{\Gamma_{VIB} = \Gamma_{3N} - \Gamma_T - \Gamma_R} = 2A_1 + B_1$

So the three normal modes of vibration for water have the symmetries A_1, A_1 and B_1.

We now have a general method for determining all of the fundamental modes of vibration for a molecule and expressing these modes in the shorthand language of Mulliken symbols. This is one of the exercises that you will be tested on in Exam 1. The best way to become confident with this method is to practice as many possible examples as you can!

Rule of mutual exclusion

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.

The rule arises because in a centrosymmetric point group, IR active modes, which must transform according to the same irreducible representation generated by one of the components of the dipole moment vector (x, y or z), must be of *ungerade* (u) symmetry, i.e. their character under inversion is -1, while Raman active modes, which transform according to the symmetry of the polarizability tensor (product of two coordinates), must be of *gerade* (g) symmetry since their character under inversion is +1. Thus, in the character table there is no irreducible representation that spans both IR and Raman active modes, and so there is no overlap between the two spectra.

This does not mean that a vibrational mode which is not Raman active must be IR active: in fact, it is still possible that a mode of a particular symmetry is neither Raman nor IR active. Such spectroscopically "silent" or "inactive" modes exist in molecules such as ethylene (C_2H_4), benzene (C_6H_6) and the tetrachloroplatinate ion ($PtCl_4^{2-}$).

Reference 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.
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

KAHE

d. The change in energy levels of an atom when placed in non-uniform electric field

12. The energy level belongs to En=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 C3v point group

a. acetylene b. water c**. ammonia** d. Boron trichloride

17. For a pyramidal molecule with point group C3v 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. 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)

Distinguish between vertical plane and horizontal plane.

(ii) Prove that $C_2(x)$
$C_2(y) = C_2(z)$.

(iii) Distinguish between vertical plane and horizontal plane.
(iv) 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
COIMBATORE-21
I M.SC CHEMISTRY (2019-2021 BATCH)
SUBJECT: PHYSICAL CHEMISTRY-I (QUANTUM CHEMISTRY AND GROUP THEORY)
SUBJECT CODE: 19CHP103
MULTIPLE CHOICE QUESTIONS(EACH QUESTION CARRY ONE MARK)
UNIT-5

S. NO	Question	Option A	Option B	Option C	Option D	Answer
1	For a planar molecule with point group D_{3h} the number of theoretically predicted IRfundamental 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

KAHE

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

KAHE

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	Overtones rule	Mutual exclusion principle

KAHE

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 0r 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

KAHE

33	As per the Great Orthogonality theorem, the sum of the squares of the characters in a givenirreducible 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

KAHE

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 Td 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

KAHE

Reg. No................................

[15CHP103]

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................................

[17CHP103]

KARPAGAM UNIVERSITY

Karpagam Academy of Higher Education
(Established Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(For the candidates admitted from 2017 onwards)

M.Sc., DEGREE EXAMINATION, NOVEMBER 2017

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. Explain black body radiation and photoelectric effect.

Or

b. Write the postulates of quantum mechanics.

22. a. For a particle in one dimensional box , show that $\Psi = A \sin \frac{n\pi}{L} x$ and $E = \frac{n^2h^2}{8mL^2}$.

Or

b. Discuss the quantum mechanical treatment for a harmonic oscillator.

23. a. What is radial distribution? Explain its importance for finding appropriate solution for Schrodinger equation.

Or

b. Explain perturbation theory.

24. a. Explain how point groups are predicted for allene and H_2O_2 molecules?

Or

b. Discuss how identity, reflection and proper rotation operations are described by a matrix?

25. a. Explain the rules of irreducible representation.

Or

b. Discuss how group theory concepts can be used to predict the modes of vibration in CO_3^{2-} ion?

PART C (1 x 10 = 10 Marks)
(Compulsory)

26. Explain how C3v point group character table can be constructed?

Reg. No................................

[18CHP103]

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
(Established Under Section 3 of UGC Act, 1956)
Pollachi Main Road, Eachanari Post, Coimbatore – 641 021
(For the candidates admitted from 2018 onwards)

M.Sc., DEGREE EXAMINATION, NOVEMBER 2018

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. Write a short note on photoelectric effect.

Or

b. Describe the linear operator with an suitable example.

22. a. Explain the separation of variables in Schrodinger equation.

Or

b. Write a short note on rigid rotator model for diatomic molecule.

23. a. Discuss the probability density and radial distribution functions.

Or

b. Describe a brief note on Perturbation theory.

24. a. Define group. Write the basic properties of a group.

Or

b. Discuss the construction of character table for C_{2V}.

25. a. Explain the Great Orthogonality theorem and its consequences.

Or

b. Illustrate with an suitable example for Mutual Exclusion Rule.

PART C (1 x 10 = 10 Marks)
(Compulsory)

26. Schrodinger equation to a particle in one dimensional box.

Reg. No.................................

[14CHP103]

KARPAGAM UNIVERSITY
(Under Section 3 of UGC Act 1956)
COIMBATORE – 641 021
(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 proof 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:
$S_4^4 = E, \quad S_3^3 = \sigma_h, \quad S_5^4 = C_5^4, S_4^2 = C_2$
(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?

Reg. No………………. **[19CHP103]**

KARPAGAM ACADEMY OF HIGHEREDUCATION
COIMBATORE-21

(For the candidate admitted from 2019 onwards)

DEPARTMENT OF CHEMISTRY
M.Sc DEGREE EXAMINATION-September 2019
Internal-I

PHYSICAL CHEMISTRY-I

DATE: **SUBJECT CODE: 19CHP103**

TIME: 2.00 HRS **TOTAL: 50 MARKS**

PART-A (20x1=20 MARKS)
ANSWER ALL THE QUESTIONS

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
a. Atomic orbital b. Molecular orbital c. Nodal plane d. Median lobes

2. This involves with the knowledge of probability
a. Quantum mechanics b. Classical mechanics c. Newtonian mechanics d. Fluid mechanics

3. The knowledge of quantum mechanics usually involves knowledge of
a. Probability b. certainties c. uncertainties d. possibility

4. Classical mechanics and quantum mechanics tend to give the same results when systems are in highly excited quantum states. This is
a. Correspondence principle b. Bohr’s theory
c. Rutherford theory d. Paulis exclusion principle

5. The energy levels of the particle in the box are
a. quantized b. randomized c. dispersed d. Not-quantised

6. In quantum mechanics the state of a system is defined by
a. Wave function b. P,V, T c. Gaseous laws d. Law of mass action

7. Simultaneous specification of position and momentum is impossible for a microscopic particle. This is
a.Stefan Boltzmann law b. Weins displacement law
c. Planck’s law d. Heisenberg uncertainty principle

8. According to Newton’s second law of motion
a. F = ma b.V = ma c.F = mv d.F = Pv

9. According to Hooke’s law the force ‘f’ acting on a molecule is given by

a. –kx b. mgh c. mv d. ½ mv

10. 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

11. The quantum number ‘n’ is called

a. Principal quantum number b. Azimuthal quantum number

c. Magnetic quantum number d. Angular momentum quantum number

12. In the particle in one dimensional problem, the property of orthogonality between any two different states ensures that

a. The various states are truly independent

b. The various states are dependent

c. One state is independent and the other is dependent

d. All are dependent and still do not interfere with each other

13. 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

14. Two atoms of mass m1 and m2 rigidly joined by a weightless link of length R is a

a. Rigid rotator b. Simple harmonic oscillator

c. Particle in one dimensional box d. Particle in three dimensional box

15. The theory of rigid rotor in space is useful in dealing with

a. Rotational spectra of diatomic molecules

b. Vibration spectra of diatomic molecules

c. IR spectra of diatomic molecules

d. Raman spectra of diatomic molecules

16. A diatomic molecule in space where the bond length is assumed to remain unchanged during rotation is a

a. Rigid rotator b. Simple harmonic oscillator

c. Particle in one dimensional box d. Angular momentum

17. Time relation between Ψ and $E_k$is

a. $\hat{E}_k\Psi= h^2/2m\ \Psi$ b. $\hat{E}_k\Psi= h^2k^2/2m\ \Psi$ c. $\hat{E}_k\Psi= h^2k^2/m\ \Psi$ d. $\hat{E}_k\Psi= h^2k^2/m^2\ \Psi$

18. Which of the following are eigen functions of $\hat{A}^2$?

a. Ψ_1 and Ψ_2 b.Ψ_2 and not Ψ_1 c.Ψ_1 and not Ψ_2 d.Neither Ψ_1 and Ψ_2

19. The expectation value of A for the state $\Psi=(^{3}\ \Psi_1 +^{4}\ \Psi_2)/5$ is

a. -0.32 b. zero c. 0.75 d. 0.96

20. Throughout $0< x < L$, the wave function

a. Can be chosen to be real b. is exponentially decaying
c. is generally complex d. is zero

PART –B (3 X2=6 MARKS)

ANSWER ALL THE QUESTIONS

21. What is meant by Black body radiation?

22. What is Photoelectric effect?

23. Explain Laplacian operator?

PART –B (5 X6=30 MARKS)

ANSWER ALL THE QUESTIONS

24. a) Give an explanatory note on time dependent Schrodinger equation.

OR

b) S.T. Wein’s and Rayleigh Jeans’s law are the limiting cases of Planck’s expression. Justify.

25.a) Write a note on Operator?

OR

b). Compare the classical mechanics and quantum mechanics within three dimensional box.

26.a).Solve of Schrodinger equation for one-dimensional harmonic oscillator.

OR

b). Write a note on spherically symmetric potential of the Hamiltonian for H-Like systems?

Reg. No………………. **[19CHP103]**

KARPAGAM ACADEMY OF HIGHEREDUCATION
COIMBATORE-21

(For the candidate admitted from 2019 onwards)

DEPARTMENT OF CHEMISTRY

M.Sc DEGREE EXAMINATION-September 2019

Internal-I

PHYSICAL CHEMISTRY-I

DATE: **SUBJECT CODE: 19CHP103**

TIME: 2.00 HRS **TOTAL: 50 MARKS**

PART-A (20x1=20 MARKS)
ANSWER ALL THE QUESTIONS

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

a. **Atomic orbital** b. Molecular orbital c. Nodal plane d. Median lobes

2. This involves with the knowledge of probability

a. **Quantum mechanics** b. Classical mechanics c. Newtonian mechanics d. Fluid mechanics

3. The knowledge of quantum mechanics usually involves knowledge of

a**. Probability** b. certainties c. uncertainties d. possibility

4. Classical mechanics and quantum mechanics tend to give the same results when systems are in highly excited quantum states. This is

a. **Correspondence principle** b. Bohr’s theory
c. Rutherford theory d. Paulis exclusion principle

5. The energy levels of the particle in the box are

a. **quantized** b. randomized c. dispersed d. Not-quantised

6. In quantum mechanics the state of a system is defined by

a. **Wave function** b. P,V, T c. Gaseous laws d. Law of mass action

7. Simultaneous specification of position and momentum is impossible for a microscopic particle. This is

a.Stefan Boltzmann law b. Weins displacement law
c. Planck’s law d. **Heisenberg uncertainty principle**

8. According to Newton’s second law of motion

a**. F = ma** b.V = ma c.F = mv d.F = Pv

9. According to Hooke’s law the force ‘f’ acting on a molecule is given by

a. **–kx** b. mgh c. mv d. ½ mv

10. 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

11. The quantum number ‘n’ is called

a. **Principal quantum number** b. Azimuthal quantum number
c. Magnetic quantum number d. Angular momentum quantum number

12. In the particle in one dimensional problem, the property of orthogonality between any two different states ensures that
a. **The various states are truly independent**
b. The various states are dependent
c. One state is independent and the other is dependent
d. All are dependent and still do not interfere with each other

13. 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

14. Two atoms of mass m1 and m2 rigidly joined by a weightless link of length R is a
a. **Rigid rotator** b. Simple harmonic oscillator
c. Particle in one dimensional box d. Particle in three dimensional box

15. The theory of rigid rotor in space is useful in dealing with
a. **Rotational spectra of diatomic molecules**
b. Vibration spectra of diatomic molecules
c. IR spectra of diatomic molecules
d. Raman spectra of diatomic molecules

16. A diatomic molecule in space where the bond length is assumed to remain unchanged during rotation is a
a. **Rigid rotator** b. Simple harmonic oscillator
c. Particle in one dimensional box d. Angular momentum

17. Time relation between Ψ and $E_k$is
a. $\hat{E}_k\Psi= h^2/2m\ \Psi$ b. **$\hat{E}_k\Psi= h^2k^2/2m\ \Psi$** c. $\hat{E}_k\Psi= h^2k^2/m\ \Psi$ d. $\hat{E}_k\Psi= h^2k^2/m^2\ \Psi$

18. Which of the following are eigen functions of $\hat{A}^2$?
a. **Ψ_1 and Ψ_2** b.Ψ_2 and not Ψ_1 c.Ψ_1 and not Ψ_2 d.Neither Ψ_1 and Ψ_2

19. The expectation value of A for the state $\Psi=(^{3}\ \Psi_1 +^{4}\ \Psi_2)/5$ is
a. -0.32 b. zero c. 0.75 d**. 0.96**

20. Throughout 0< x < L, the wave function
a. **Can be chosen to be real** b. is exponentially decaying
c. is generally complex d. is zero

PART –B (3 X2=6 MARKS)

ANSWER ALL THE QUESTIONS

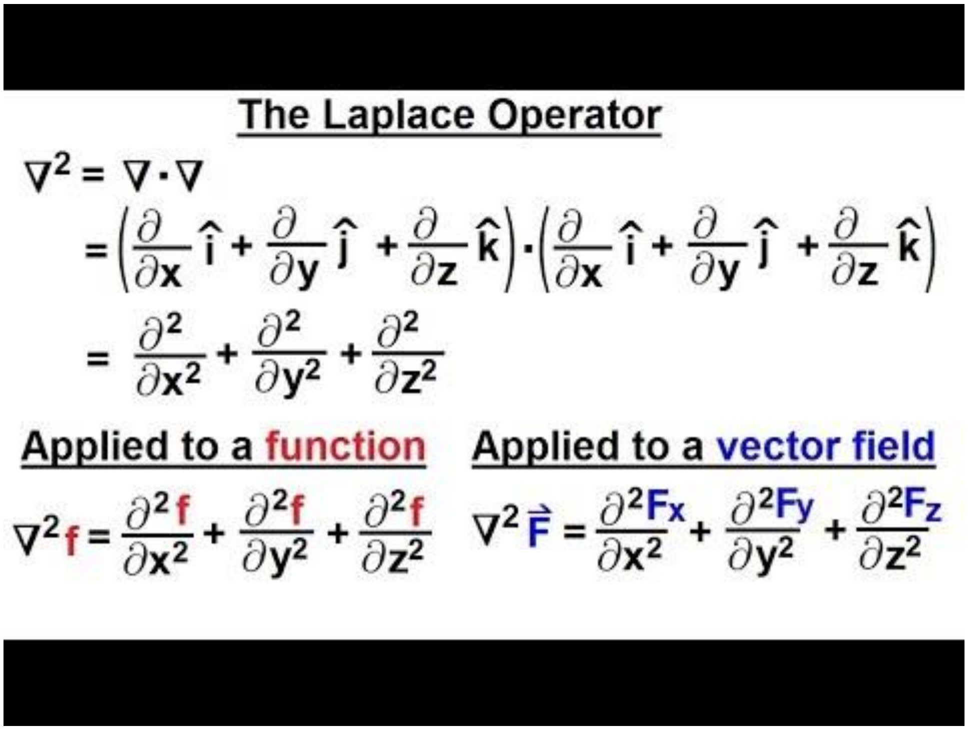
21. What is meant by Black body radiation?

A **blackbody** (sometimes spelled "**black body**") is a theoretically ideal radiator and absorber of energy at all electromagnetic wavelength s. The term comes from the fact that a cold **blackbody** appears visually **black**. The energy emitted by a **blackbody** is called **blackbody radiation**.

22. What is Photoelectric effect?

The photoelectric effect is the emission of electrons or other free carriers when light hits a material. Electrons emitted in this manner can be called photoelectrons. This phenomenon is commonly studied in electronic physics and in fields of chemistry such as quantum chemistry and electrochemistry.

23. Explain Laplacian operator?



The Laplace Operator

$$\nabla^2 = \nabla \cdot \nabla$$

$$= \left(\frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}\right) \cdot \left(\frac{\partial}{\partial x}\hat{i} + \frac{\partial}{\partial y}\hat{j} + \frac{\partial}{\partial z}\hat{k}\right)$$

$$= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Applied to a function

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}$$

Applied to a vector field

$$\nabla^2 \vec{F} = \frac{\partial^2 F_x}{\partial x^2} + \frac{\partial^2 F_y}{\partial y^2} + \frac{\partial^2 F_z}{\partial z^2}$$

PART –B (5 X6=30 MARKS)

ANSWER ALL THE QUESTIONS

24. a) Give an explanatory note on time dependent Schrodinger equation.

The Time-Dependent Schrödinger Equation

We are now ready to consider the time-dependent Schrödinger equation. Although we were able to derive the single-particle time-independent Schrödinger equation starting from the classical wave equation and the de Broglie relation, the time-dependent Schrödinger equation cannot be derived using elementary methods and is generally given as a postulate of quantum mechanics. It is possible to show that the time-dependent equation is at least *reasonable* if not derivable, but the arguments are rather involved (cf. Merzbacher [2], Section 3.2; Levine [3], Section 1.4).

The single-particle three-dimensional time-dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t) \quad (21)$$

where V is assumed to be a real function and represents the potential energy of the system (a complex function V will act as a source or sink for probability, as shown in Merzbacher [2], problem 4.1). *Wave Mechanics* is the branch of quantum mechanics with equation (21) as its dynamical law. Note that equation (21) does not yet account for spin or relativistic effects.

Of course the time-dependent equation can be used to derive the time-independent equation. If we write the wavefunction as a product of spatial and temporal terms, $\psi(\mathbf{r},t) = \psi(\mathbf{r})f(t)$, then equation (21) becomes

$$\psi(\mathbf{r})i\hbar\frac{df(t)}{dt} = f(t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) \tag{22}$$

or

$$\frac{i\hbar}{f(t)}\frac{df}{dt} = \frac{1}{\psi(\mathbf{r})}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) \tag{23}$$

Since the left-hand side is a function of t only and the right hand side is a function of $\mathbf{r}$ only, the two sides must equal a constant. If we tentatively designate this constant E (since the right-hand side clearly must have the dimensions of energy), then we extract two ordinary differential equations, namely

$$\frac{1}{f(t)}\frac{df(t)}{dt} = -\frac{iE}{\hbar} \tag{24}$$

and

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{25}$$

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

$$f(t) = e^{-iEt/\hbar} \tag{26}$$

The Hamiltonian in equation (25) is a Hermitian operator, and the eigenvalues of a Hermitian operator must be real, so E is real. This means that the solutions $f(t)$ are purely oscillatory, since $f(t)$ never changes in magnitude (recall Euler's formula $e^{\pm i\theta} = cos\theta \pm i\ sin\theta$). Thus if

$$\psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar} \tag{27}$$

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

$$|\psi(\mathbf{r}, t)|^2 = \psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t) = e^{iEt/\hbar}\psi^*(\mathbf{r})e^{-iEt/\hbar}\psi(\mathbf{r}) = \psi^*(\mathbf{r})\psi(\mathbf{r}) \tag{28}$$

Secondly, the expectation value for any time-independent operator is also time-independent, if $\psi(\mathbf{r}, t)$ satisfies equation (27). By the same reasoning applied above,

$$< A >= \int \psi^*(\mathbf{r}, t)\hat{A}\psi(\mathbf{r}, t) = \int \psi^*(\mathbf{r})\hat{A}\psi(\mathbf{r}) \tag{29}$$

For these reasons, wave functions of the form (27) are called *stationary states*. The state $\psi(\mathbf{r}, t)$ is ``stationary,'' but the particle it describes is not!

Of course equation (27) represents a particular solution to equation (21). The general solution to equation (21) will be a linear combination of these particular solutions, i.e.

$$\psi(\mathbf{r},t) = \sum_i c_i e^{-iE_i t/\hbar}\psi_i(\mathbf{r})$$

OR

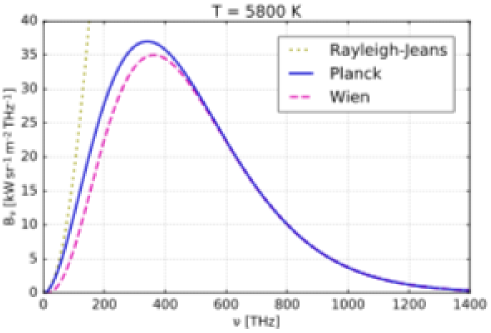
b) S.T. Wein's and Rayleigh Jeans's law are the limiting cases of Planck's expression. Justify.

In physics, the **Rayleigh–Jeans Law** is an approximation to the spectral radiance of electromagnetic radiation as a function of wavelength from a black body at a given temperature through classical arguments. For wavelength λ, it is:

$$B_\lambda(T) = \frac{2ck_B T}{\lambda^4},$$

where B_λ is the spectral radiance, the power emitted per unit emitting area, per steradian, per unit wavelength; c is the speed of light; k_B is the Boltzmann constant; and T is the temperature in kelvins. For frequency ν, the expression is instead

$$B_\nu(T) = \frac{2\nu^2 k_B T}{c^2}.$$



Comparison of Rayleigh–Jeans law with Wien approximation and Planck's law, for a body of 5800 K temperature.

The Rayleigh–Jeans law agrees with experimental results at large wavelengths (low frequencies) but strongly disagrees at short wavelengths (high frequencies). This inconsistency between observations and the predictions of classical physics is commonly known as the ultraviolet catastrophe.[1][2] Its resolution in 1900 with the derivation by Max Planck of Planck's law, which gives the correct radiation at all frequencies, was a foundational aspect of the development of quantum mechanics in the early 20th century.

In 1900, the British physicist Lord Rayleigh derived the λ^{-4} dependence of the Rayleigh–Jeans law based on classical physical arguments and empirical facts.[1] A more complete derivation, which included the proportionality constant, was presented by Rayleigh and Sir James Jeans in 1905. The Rayleigh–Jeans law revealed an important error in physics theory of the time. The law predicted an energy output that diverges towards infinity as wavelength approaches zero (as frequency tends to infinity). Measurements of the spectral emission of actual black bodies revealed that the emission agreed with the Rayleigh–Jeans law at low frequencies but diverged at high frequencies; reaching a maximum and then falling with frequency, so the total energy emitted is finite.

Comparison to Planck's law

In 1900 Max Planck empirically obtained an expression for black-body radiation expressed in terms of wavelength $\lambda = c/\nu$ (Planck's law):

$$B_\lambda(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_\mathrm{B} T}} - 1},$$

where h is the Planck constant and k_B the Boltzmann constant. The Planck's law does not suffer from an ultraviolet catastrophe, and agrees well with the experimental data, but its full significance (which ultimately led to quantum theory) was only appreciated several years later. Since,

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots.$$

then in the limit of high temperatures or long wavelengths, the term in the exponential becomes small, and the exponential is well approximated with the Taylor polynomial's first-order term,

$$e^{\frac{hc}{\lambda k_\mathrm{B} T}} \approx 1 + \frac{hc}{\lambda k_\mathrm{B} T}.$$

So,

$$\frac{1}{e^{\frac{hc}{\lambda k_\mathrm{B} T}} - 1} \approx \frac{1}{\frac{hc}{\lambda k_\mathrm{B} T}} = \frac{\lambda k_\mathrm{B} T}{hc}.$$

This results in Planck's blackbody formula reducing to

$$B_\lambda(T) = \frac{2ck_\mathrm{B} T}{\lambda^4},$$

which is identical to the classically derived Rayleigh–Jeans expression.

The same argument can be applied to the blackbody radiation expressed in terms of frequency $\nu = c/\lambda$. In the limit of small frequencies, that is $h\nu \ll k_\mathrm{B} T$,

$$B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{k_\mathrm{B} T}} - 1} \approx \frac{2h\nu^3}{c^2} \cdot \frac{k_\mathrm{B} T}{h\nu} = \frac{2\nu^2 k_\mathrm{B} T}{c^2}.$$

This last expression is the Rayleigh–Jeans law in the limit of small frequencies.

25.a) Write a note on Operator?

Operators

Levine [3] defines an *operator* as ``a rule that transforms a given function into another function" (p. 33). The differentation operator d/dx is an example--it transforms a differentiable function $f(x)$ into another function $f'(x)$. Other examples include integration, the square root, and so forth. Numbers can also be considered as operators (they multiply a function). McQuarrie [1] gives an even more general definition for an operator: ``An *operator* is a symbol that tells you to do something with whatever follows the symbol" (p. 79). Perhaps this definition is more appropriate if we want to refer to the $\hat{C}_3$ operator acting on NH_3, for example.

Linear Operators

Almost all operators encountered in quantum mechanics are *linear operators*. A linear operator is an operator which satisfies the following two conditions:

$$\hat{A}(f+g) = \hat{A}f + \hat{A}g \tag{43}$$

$$\hat{A}(cf) = c\hat{A}f \tag{44}$$

where c is a constant and f and g are functions. As an example, consider the operators d/dx and $()^2$. We can see that d/dx is a linear operator because

$$(d/dx)[f(x)+g(x)] = (d/dx)f(x) + (d/dx)g(x) \tag{45}$$

$$(d/dx)[cf(x)] = c\,(d/dx)f(x) \tag{46}$$

However, $()^2$ is not a linear operator because

$$(f(x)+g(x))^2 \neq (f(x))^2 + (g(x))^2 \tag{47}$$

The only other category of operators relevant to quantum mechanics is the set of *antilinear* operators, for which

$$\hat{A}(\lambda f + \mu g) = \lambda^* \hat{A}f + \mu^* \hat{A}g \tag{48}$$

Time-reversal operators are antilinear (cf. Merzbacher [2], section 16-11).

OR

b). Compare the classical mechanics and quantum mechanics within three dimensional box.

Quantum mechanics and classical physics

Predictions of quantum mechanics have been verified experimentally to an extremely high degree of accuracy.[47] According to the correspondence principle between classical and quantum mechanics, all objects obey the laws of quantum mechanics, and classical mechanics is just an approximation for large systems of objects (or astatistical quantum mechanics of a large collection of particles).[48] The laws of classical mechanics thus follow from the laws of quantum mechanics as a statistical average at the limit of large systems or large quantum numbers.[49] However, chaotic systems do not have good quantum numbers, and quantum chaos studies the relationship between classical and quantum descriptions in these systems.

Quantum coherence is an essential difference between classical and quantum theories as illustrated by the Einstein–Podolsky–Rosen(EPR)paradox–anattackonacertainphilosophicalinterpretationofquantummechanicsbyanappeal to local realism.[50] Quantum interferenceinvolves adding together *probability amplitudes*, whereas classical "waves" inferthatthereisanaddingtogetherof*intensities*.Formicroscopicbodies,theextensionofthesystemismuchsmaller thanthecoherencelength,whichgivesrisetolong-rangeentanglementandothernonlocalphenomenacharacteristicof quantumsystems.[51] Quantumcoherenceisnottypicallyevidentatmacroscopicscales,thoughanexceptiontothisrule mayoccuratextremelylowtemperatures(i.e.approachingabsolutezero)atwhichquantumbehaviormaymanifestitself macroscopically.[52]Thisisinaccordancewiththefollowingobservations:

- Many macroscopic properties of a classical system are a direct consequence of the quantum behavior of its parts. For example, the stability of bulk matter (consisting of atoms and molecules which would quickly collapse under electric forces alone), the rigidity of solids, and the mechanical, thermal, chemical, optical and magnetic properties of matter are all results of the interaction of electric charges under the rules of quantum mechanics.
- While the seemingly "exotic" behavior of matter posited by quantum mechanics and relativity theory become more apparent when dealing with particles of extremely small size or velocities approaching the speed of light, the laws of classical, often considered "Newtonian", physics remain accurate in predicting the behavior of the vast majority of "large" objects (on the order of the size of large molecules or bigger) at velocities much smaller than the velocity of light.[54]

26.a).Solve of Schrodinger equation for one-dimensional harmonic oscillator.

Harmonic oscillator

As in the classical case, the potential for the quantum harmonic oscillator is given by

$$V(x) = \frac{1}{2} m\omega^2 x^2.$$

This problem can either be treated by directly solving the Schrödinger equation, which is not trivial, or by using the more elegant "ladder method" first proposed by Paul Dirac. The eigenstates are given by

$$\psi_n(x) = \sqrt{\frac{1}{2^n\, n!}} \cdot \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \cdot e^{-\frac{m\omega x^2}{2\hbar}} \cdot H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right),$$

$$n = 0, 1, 2, \ldots.$$

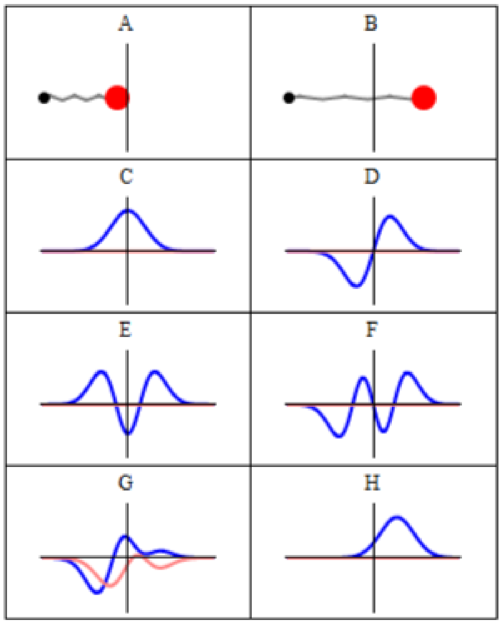
where H_n are the Hermite polynomials

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}\left(e^{-x^2}\right),$$

and the corresponding energy levels are

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

This is another example illustrating the quantification of energy for bound states.



Some trajectories of a harmonic oscillator (i.e. a ball attached to a spring) in classical mechanics (A-B) and quantum mechanics (C-H). In quantum mechanics, the position of the ball is represented by a wave (called the wave function), with the real part shown in blue and the imaginary part shown in red. Some of the trajectories (such as C, D, E, and F) are standing waves (or "stationary states"). Each standing-wave frequency is proportional to a possible energy level of the oscillator. This "energy quantization" does not occur in classical physics, where the oscillator can have *any* energy.

Step potential

The potential in this case is given by:

$$V(x) = \begin{cases} 0, & x < 0, \\ V_0, & x \geq 0. \end{cases}$$

The solutions are superpositions of left- and right-moving waves:

$$\psi_1(x) = \frac{1}{\sqrt{k_1}}\left(A_{\rightarrow}e^{ik_1x} + A_{\leftarrow}e^{-ik_1x}\right) \qquad x < 0$$

and

$$\psi_2(x) = \frac{1}{\sqrt{k_2}}\left(B_{\rightarrow}e^{ik_2x} + B_{\leftarrow}e^{-ik_2x}\right) \qquad x > 0,$$

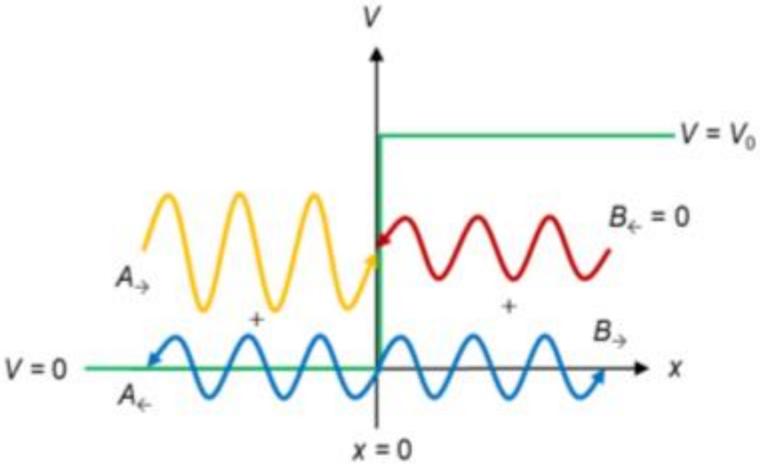
with coefficients A and B determined from the boundary conditions and by imposing a continuous derivative on the solution, and where the wave vectors are related to the energy via

$$k_1 = \sqrt{2mE/\hbar^2}$$

and

$$k_2 = \sqrt{2m(E - V_0)/\hbar^2}\,.$$

Each term of the solution can be interpreted as an incident, reflected, or transmitted component of the wave, allowing the calculation of transmission and reflection coefficients. Notably, in contrast to classical mechanics, incident particles with energies greater than the potential step are partially reflected.



Scattering at a finite potential step of height V_0, shown in green. The amplitudes and direction of left- and right-moving waves are indicated. Yellow is the incident wave, blue are reflected and transmitted waves, red does not occur. $E > V_0$ for this figure.

OR

b). Write a note on spherically symmetric potential of the Hamiltonian for H-Like systems?

Hydrogen-like atoms

A hydrogenic (hydrogen-like) atom is a two-particle system consisting of a nucleus and an electron. The two particles interact through the potential given by Coulomb's law:

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$$

where

- ε_0 is the permittivity of the vacuum,
- Z is the atomic number (eZ is the charge of the nucleus),
- e is the elementary charge (charge of the electron),
- r is the distance between the electron and the nucleus.

The mass m_0, introduced above, is the reduced mass of the system. Because the electron mass is about 1836 times smaller than the mass of the lightest nucleus (the proton), the value of m_0 is very close to the mass of the electron m_e for all hydrogenic atoms. In the remaining of the article we make the approximation $m_0 = m_e$. Since m_e will appear explicitly in the formulas it will be easy to correct for this approximation if necessary.

In order to simplify the Schrödinger equation, we introduce the following constants that define the atomic unit of energy and length, respectively,

$$E_\mathrm{h} = m_\mathrm{e}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \quad \text{and} \quad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_\mathrm{e}e^2}.$$

Substitute $y = Zr/a_0$ and $W = E/(Z^2 E_\mathrm{h})$ into the radial Schrödinger equation given above. This gives an equation in which all natural constants are hidden,

$$\left[-\frac{1}{2}\frac{d^2}{dy^2} + \frac{1}{2}\frac{l(l+1)}{y^2} - \frac{1}{y}\right]u_l = Wu_l.$$

Two classes of solutions of this equation exist: (i) W is negative, the corresponding eigenfunctions are square integrable and the values of W are quantized (discrete spectrum). (ii) W is non-negative. Every real non-negative value of W is physically allowed (continuous spectrum), the corresponding eigenfunctions are non-square integrable. In the remaining part of this article only class (i) solutions will be considered. The wavefunctions are known as bound states, in contrast to the class (ii) solutions that are known as *scattering states*.

For negative W the quantity $\alpha \equiv 2\sqrt{-2W}$ is real and positive. The scaling of y, i.e., substitution of $x \equiv \alpha y$ gives the Schrödinger equation:

$$\left[\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2} + \frac{2}{\alpha x} - \frac{1}{4}\right]u_l = 0, \quad \text{with } x \geq 0.$$

For $x \to \infty$ the inverse powers of x are negligible and a solution for large x is $\exp[-x/2]$. The other solution, $\exp[x/2]$, is physically non-acceptable. For $x \to 0$ the inverse square power dominates and a solution for small x is x^{l+1}. The other solution, x^{-l}, is physically non-acceptable. Hence, to obtain a full range solution we substitute

$$u_l(x) = x^{l+1} e^{-x/2} f_l(x).$$

The equation for $f_l(x)$ becomes,

$$\left[x\frac{d^2}{dx^2} + (2l+2-x)\frac{d}{dx} + (\nu - l - 1)\right] f_l(x) = 0 \quad \text{with} \quad \nu = (-2W)^{-\frac{1}{2}}.$$

Provided $\nu - l - 1$ is a non-negative integer, say k, this equation has polynomial solutions written as

$$L_k^{(2l+1)}(x), \qquad k = 0, 1, \ldots,$$

which are generalized Laguerre polynomials of order k. We will take the convention for generalized Laguerre polynomials of Abramowitz and Stegun.[2] Note that the Laguerre polynomials given in many quantum mechanical textbooks, for instance the book of Messiah,[1] are those of Abramowitz and Stegun multiplied by a factor $(2l+1+k)!$ The definition given in this Wikipedia article coincides with the one of Abramowitz and Stegun.

The energy becomes

$$W = -\frac{1}{2n^2} \quad \text{with} \quad n \equiv k + l + 1.$$

The principal quantum number n satisfies $n \geq l + 1$, or $l \leq n - 1$. Since $\alpha = 2/n$, the total radial wavefunction is

$$R_{nl}(r) = N_{nl} \left(\frac{2Zr}{na_0}\right)^l e^{-\frac{Zr}{na_0}} \; L_{n-l-1}^{(2l+1)} \left(\frac{2Zr}{na_0}\right),$$

with normalization constant

$$N_{nl} = \left[\left(\frac{2Z}{na_0}\right)^3 \cdot \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{\frac{1}{2}}$$

which belongs to the energy

$$E = -\frac{Z^2}{2n^2} E_{\mathrm{h}}, \qquad n = 1, 2, \ldots.$$

In the computation of the normalization constant use was made of the integral [3]

$$\int_0^\infty x^{2l+2} e^{-x} \left[L_{n-l-1}^{(2l+1)}(x)\right]^2 dx = \frac{2n(n+l)!}{(n-l-1)!}.$$

Reg. No………………. **[19CHP103]**

KARPAGAM ACADEMY OF HIGHEREDUCATION
COIMBATORE-21
(For the candidate admitted from 2019 onwards)
DEPARTMENT OF CHEMISTRY
M.Sc DEGREE EXAMINATION-NOVEMBER 2019
PHYSICAL CHEMISTRY-I
INTERNAL TEST-II

DATE: **SUBJECT CODE: 19CHP103**
TIME: 2.00 HRS **TOTAL: 50 MARKS**

PART-A (20x1=20 MARKS)
ANSWER ALL THE QUESTIONS

1. The structure of methane is
a. Linear b.Triangular planar c. tetrahedral d. Octahedral

2. Structure of phosphorous pentachloride is
a. Linear b.Trigonal bipyramidal c. Tetrahedral d. Octahedral

3. Example for a linear molecule
a. $BeCl_2$ b. boron trifluoride c. methane d. phosphorous pentachloride

4. Example for triangular planar molecule
a. $BeCl_2$ b. boron trifluoride c. methane d. phosphorous pentachloride

5. For the C_{3v} point group, the order of the group is
a. Four b. five c. six d. three

6. Formaldehyde has
a. Three sigma bonding molecular orbitals b.Four sigma bonding molecular orbitals
c.Five sigma bonding molecular orbitals d.Six sigma bonding molecular orbitals

7. In the C_{2v} point group the ‘z’ coordinate transformers is
a. A1 b. A2 c. B1 d. B2

8. The symmetry or antisymmetry is with respect to
a. Subsidiary axis b. Principal axis c.Vertical axis
d.Horizontal axis

9. One of the following is an geometric operation when performed on the molecule, give rise to an indistinguishable configuration of the same molecule
a. Diffraction b. interference c. polarization d.inversion

10. If the symmetry element is the ‘identity element” 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

11.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

12.If the symmetry element is the ‘proper axis 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

13. The number of elements present in C_{3v} point group
a. Four b. five c. six d.three

14. The order of the group is denoted by
a. h b. E c. I d. j

15. The character of any two irreducible representations of a group are
a. orthogonal b. diagonal c. parabola d. hyperbola

16. In C_{2v} point group the number of classes are possible
a. Four b. five c. six d.three

17. The molecule which possesses $C\alpha$ axis of symmetry is
a. Matrices b.determinants c.Space lattices d.Miller indices

18. An array of numbers arranged in rows and columns are called
a. Matrices b.determinants c.Space lattices d.Miller indices

19. A collection of the symmetry elements present in a molecule that obeys the mathematical rules for the formation of a group are called
a.Point groups b.Space groups c.Space lattices d. Miller indices

20. A square matrix will have
a. An equal number of rows and columns b. An unequal number of rows and columns
c. Only rows d.Only columns

PART-B (3x2=6 MARKS)
ANSWER ALL THE QUESTIONS

21. What is meant by Abelian group?

22. Explain Null matrix.

23. What is radial distribution function?

PART-C (3x8=24 MARKS)
ANSWER ALL THE QUESTIONS

24. a).i).What is a group?

ii). What are the cyclic, finite and infinite group's?

iii).Define class.

OR

b). i). What are the relationships between reducible and irreducible representation of the group?

ii). What are the properties of irreducible representation?

25.a). How will you construct the character table for a C_{2v} and C_{3v} point group using the great orthogonality theorem?

OR

b). Explain the symmetry selection rules for Infra-red and Raman spectra.

26. a). Write a note on Elements of Symmetry?

OR

b). Explain the great orthogonality theory and its consequences.

Reg. No………………. **[19CHP103]**

KARPAGAM ACADEMY OF HIGHEREDUCATION
COIMBATORE-21
(For the candidate admitted from 2019 onwards)
DEPARTMENT OF CHEMISTRY
M.Sc DEGREE EXAMINATION-NOVEMBER 2019
PHYSICAL CHEMISTRY-I
INTERNAL TEST-II

DATE: **SUBJECT CODE: 19CHP103**

TIME: 2.00 HRS **Answer Key** **TOTAL: 50 MARKS**

PART-A (20x1=20 MARKS)
ANSWER ALL THE QUESTIONS

1. The structure of methane is
a. Linear b.Triangular planar c. **tetrahedral** d. Octahedral

2. Structure of phosphorous pentachloride is
a. Linear b.**Trigonalbipyramidal** c. Tetrahedral d. Octahedral

3. Example for a linear molecule
a. **$BeCl_2$** b. boron trifluoride c. methane d. phosphorous pentachloride

4. Example for triangular planar molecule
a. $BeCl_2$ b. **boron trifluoride** c. methane d. phosphorous pentachloride

5. For the C_{3v} point group, the order of the group is
a. Four b. five c. **six** d. three

6. Formaldehyde has
a. **Three sigma bonding molecular orbitals** b.Four sigma bonding molecular orbitals
c.Five sigma bonding molecular orbitals d.Six sigma bonding molecular orbitals

7. In the C_{2v} point group the ‘z’ coordinate transformers is
a. **A1** b. A2 c. B1 d. B2

8. The symmetry or antisymmetry is with respect to
a. **Subsidiary axis** b. Principal axis c.Vertical axis
d.Horizontal axis

9. One of the following is an geometric operation when performed on the molecule, give rise to an indistinguishable configuration of the same molecule
a. Diffraction b. interference c. polarization d.**inversion**

10. If the symmetry element is the ‘identity element” 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

11.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

12.If the symmetry element is the ‘proper axis 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**

13. The number of elements present in C_{3v} point group

a. Four b. five c. **six** d.three

14. The order of the group is denoted by

a. **h** b. E c. I d. j

15. The character of any two irreducible representations of a group are

a. **orthogonal** b. diagonal c. parabola d. hyperbola

16. In C_{2v} point group the number of classes are possible

a. **Four** b. five c. six d.three

17. The molecule which possesses Cα axis of symmetry is

a. **Matrices** b.determinants c.Space lattices d.Miller indices

18. An array of numbers arranged in rows and columns are called

a. **Matrices** b.determinants c.Space lattices d.Miller indices

19. A collection of the symmetry elements present in a molecule that obeys the mathematical rules for the formation of a group are called

a.**Point groups** b.Space groups c.Space lattices d. Miller indices

20. A square matrix will have

a. **An equal number of rows and columns** b. An unequal number of rows and columns

c. Only rows d.Only columns

PART-B (3x2=6 MARKS)
ANSWER ALL THE QUESTIONS

21. What is meant by Abelian group?

An abelian group, also called a commutative group, is a group in which the result of applying the group operation to two group elements does not depend on the order in which they are written. That is, these are the groups that obey the axiom of commutativity.

22. Explain Null matrix.

A null matrix is basically a matrix, whose all elements are zero. In a matrix basically there are two elements, first one is diagonal matrix and another one is non-diagonal elements. In Null matrix both diagonal and off-diagonal elements are zero. Null matrix is also called zero matrix.

23. What is radial distribution function?

When the wavefunction, ψ, is squared the result is a number that is directly proportional to the probability of finding and electron at specific coordinate in 3D space. The radial portion of the wavefunction really only tells us if there is high or low probability at various distances from the nucleus (possible radii for the electrons). Multiplying this probability by the area available at that distance will give us the *Radial Distribution Function* for the given electron. The concentric spherical shells have areas equal to the surface area of a sphere which is 4πr2.

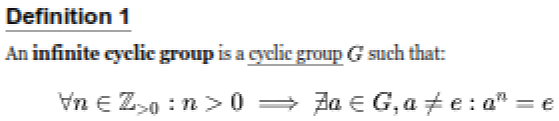
PART-C (3x8=24 MARKS)
ANSWER ALL THE QUESTIONS

24. a).i).What is a group?

ii). What are the cyclic, finite and infinite group's?

iii).Define class.

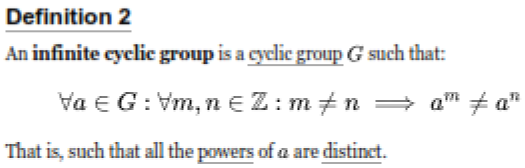
A group is a monoid each of whose elements is invertible. A group must contain at least one element, with the unique (up to isomorphism) single-element group known as the trivial group. The study of groups is known as group theory.



Definition 1

An **infinite cyclic group** is a cyclic group G such that:

$$\forall n \in \mathbb{Z}_{>0} : n > 0 \implies \nexists a \in G, a \neq e : a^n = e$$

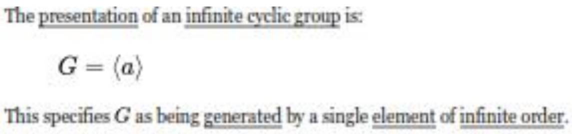


Definition 2

An **infinite cyclic group** is a cyclic group G such that:

$$\forall a \in G : \forall m, n \in \mathbb{Z} : m \neq n \implies a^m \neq a^n$$

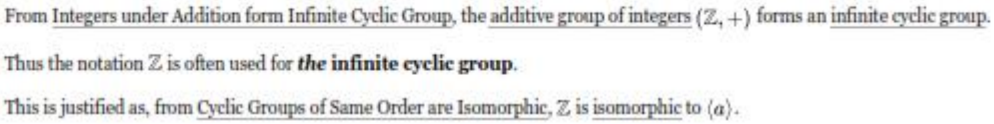
That is, such that all the powers of a are distinct.



The presentation of an infinite cyclic group is:

$$G = \langle a \rangle$$

This specifies G as being generated by a single element of infinite order.

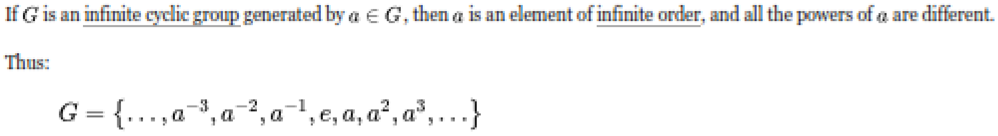


From Integers under Addition form Infinite Cyclic Group, the additive group of integers $(\mathbb{Z}, +)$ forms an infinite cyclic group.

Thus the notation $\mathbb{Z}$ is often used for ***the* infinite cyclic group**.

This is justified as, from Cyclic Groups of Same Order are Isomorphic, $\mathbb{Z}$ is isomorphic to $\langle a \rangle$.

A **cyclic group** is also known as a **free group on one generator**.



If G is an infinite cyclic group generated by $a \in G$, then a is an element of infinite order, and all the powers of a are different.

Thus:

$$G = \{\ldots, a^{-3}, a^{-2}, a^{-1}, e, a, a^2, a^3, \ldots\}$$

A class of groups is a set theoretical collection of groups satisfying the property that if *G* is in the collection then every group isomorphic to *G* is also in the collection. This concept arose from the necessity to work with a bunch of groups satisfying certain special property (for example finiteness or commutativity). Since set theory does not admit the "set of all groups", it is necessary to work with the more general concept of *class*.

OR

b). i). What are the relationships between reducible and irreducible representation of the group?

We need to know the relationship between any arbitrary reducible representation and the irreducible representations of that point group. As was mentioned in the last chapter, there is no limit to the order of a representation; that is, it may consist of matrices of any size. Some of the reducible representations that are of use in, for example, vibrational spectroscopy are of very large dimensions. Frequent use is made of the representations generated by placing three Cartesian coordinate vectors on each atom in a molecule. For an N-atomic molecule, this will give a representation consisting of $3N \times 3N$ matrices; for example, for benzene, the matrices will be of dimension 36×36. In order to handle and analyse such matrices, it is essential to reduce them to more manageable sizes; that is, to reduce them eventually to those of the irreducible representations, which are the representations of the smallest possible dimensions for any point group. How can this be done?

5.1 Reducing representations

Consider any matrix, of dimension $n \times n$ (all transformation matrices are square, since the *number* of vectors or functions is not changed by any symmetry operation):

$$\begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{bmatrix}$$

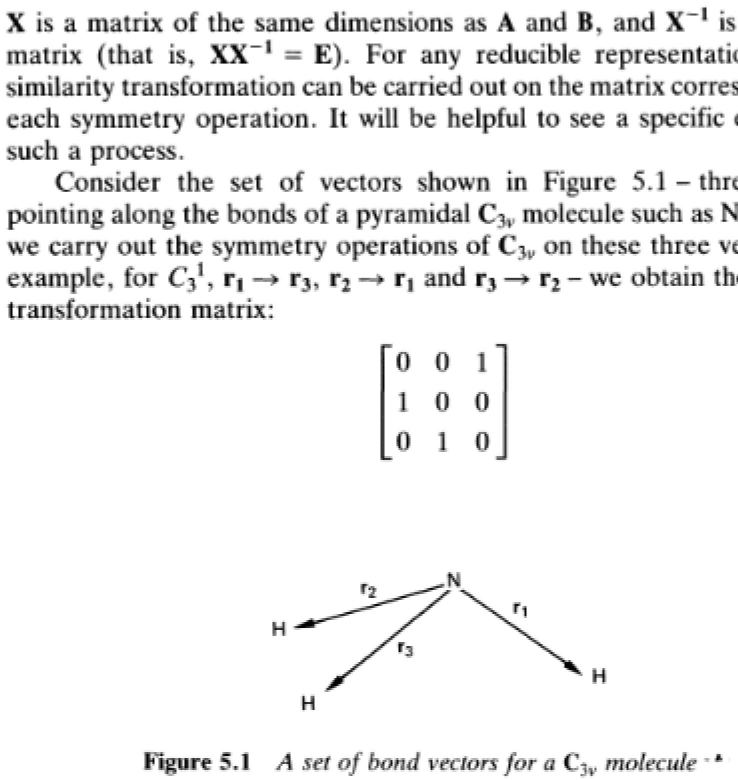
In this matrix, the zero elements (if any) will be distributed randomly about the matrix. If, however, the matrix belongs to a reducible representation, it will be possible to rearrange the matrix so that zero elements are distributed symmetrically about the diagonal. Thus, for a 3×3 matrix we might have:

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \longrightarrow \left[\begin{array}{cc:c} b_{11} & b_{12} & 0 \\ b_{21} & b_{22} & 0 \\ \hdashline 0 & 0 & b_{33} \end{array}\right]$$

The non-zero elements are now distributed in blocks along the diagonal – in this case, a 2×2 block and a 1×1 block. How is such a rearrangement brought about?

In Chapter 2, a method of defining classes of symmetry operations was described. This involved the application of similarity transformations, defined in terms of symmetry operations. It is found that matrix rearrangement can be accomplished by means of a similarity transformation of the original matrix. Thus, if $\mathbf{A}$ and $\mathbf{B}$ are the original and reduced matrices, respectively, then:

$$\mathbf{XAX}^{-1} = \mathbf{B}$$



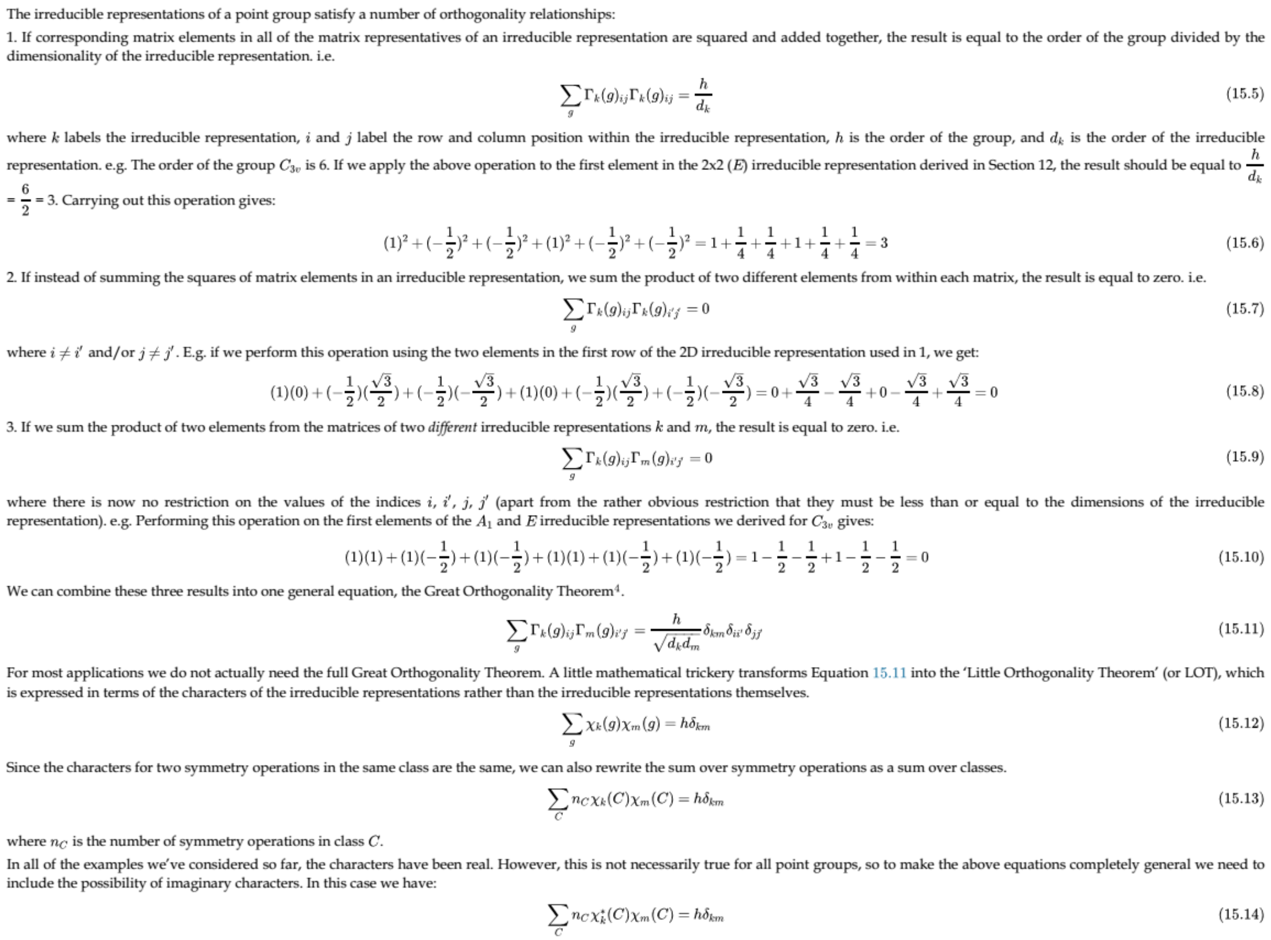
$\mathbf{X}$ is a matrix of the same dimensions as $\mathbf{A}$ and $\mathbf{B}$, and $\mathbf{X}^{-1}$ is its inverse matrix (that is, $\mathbf{XX}^{-1} = \mathbf{E}$). For any reducible representation, such a similarity transformation can be carried out on the matrix corresponding to each symmetry operation. It will be helpful to see a specific example of such a process.

Consider the set of vectors shown in Figure 5.1 – three vectors, pointing along the bonds of a pyramidal $\mathbf{C}_{3v}$ molecule such as NH_3. Now if we carry out the symmetry operations of $\mathbf{C}_{3v}$ on these three vectors – for example, for C_3^1, $\mathbf{r}_1 \rightarrow \mathbf{r}_3$, $\mathbf{r}_2 \rightarrow \mathbf{r}_1$ and $\mathbf{r}_3 \rightarrow \mathbf{r}_2$ – we obtain the following transformation matrix:

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

Figure 5.1 *A set of bond vectors for a* $\mathbf{C}_{3v}$ *molecule*

ii). What are the properties of irreducible representation



The irreducible representations of a point group satisfy a number of orthogonality relationships:

1. If corresponding matrix elements in all of the matrix representatives of an irreducible representation are squared and added together, the result is equal to the order of the group divided by the dimensionality of the irreducible representation. i.e.

$$\sum_g \Gamma_k(g)_{ij}\Gamma_k(g)_{ij} = \frac{h}{d_k} \tag{15.5}$$

where k labels the irreducible representation, i and j label the row and column position within the irreducible representation, h is the order of the group, and d_k is the order of the irreducible representation. e.g. The order of the group C_{3v} is 6. If we apply the above operation to the first element in the 2x2 (E) irreducible representation derived in Section 12, the result should be equal to $\frac{h}{d_k}$ = $\frac{6}{2}$ = 3. Carrying out this operation gives:

$$(1)^2+(-\frac{1}{2})^2+(-\frac{1}{2})^2+(1)^2+(-\frac{1}{2})^2+(-\frac{1}{2})^2 = 1+\frac{1}{4}+\frac{1}{4}+1+\frac{1}{4}+\frac{1}{4} = 3 \tag{15.6}$$

2. If instead of summing the squares of matrix elements in an irreducible representation, we sum the product of two different elements from within each matrix, the result is equal to zero. i.e.

$$\sum_g \Gamma_k(g)_{ij}\Gamma_k(g)_{i'j'} = 0 \tag{15.7}$$

where $i \neq i'$ and/or $j \neq j'$. E.g. if we perform this operation using the two elements in the first row of the 2D irreducible representation used in 1, we get:

$$(1)(0)+(-\frac{1}{2})(\frac{\sqrt{3}}{2})+(-\frac{1}{2})(-\frac{\sqrt{3}}{2})+(1)(0)+(-\frac{1}{2})(\frac{\sqrt{3}}{2})+(-\frac{1}{2})(-\frac{\sqrt{3}}{2}) = 0+\frac{\sqrt{3}}{4}-\frac{\sqrt{3}}{4}+0-\frac{\sqrt{3}}{4}+\frac{\sqrt{3}}{4} = 0 \tag{15.8}$$

3. If we sum the product of two elements from the matrices of two *different* irreducible representations k and m, the result is equal to zero. i.e.

$$\sum_g \Gamma_k(g)_{ij}\Gamma_m(g)_{i'j'} = 0 \tag{15.9}$$

where there is now no restriction on the values of the indices i, i', j, j' (apart from the rather obvious restriction that they must be less than or equal to the dimensions of the irreducible representation). e.g. Performing this operation on the first elements of the A_1 and E irreducible representations we derived for C_{3v} gives:

$$(1)(1)+(1)(-\frac{1}{2})+(1)(-\frac{1}{2})+(1)(1)+(1)(-\frac{1}{2})+(1)(-\frac{1}{2}) = 1-\frac{1}{2}-\frac{1}{2}+1-\frac{1}{2}-\frac{1}{2} = 0 \tag{15.10}$$

We can combine these three results into one general equation, the Great Orthogonality Theorem[4].

$$\sum_g \Gamma_k(g)_{ij}\Gamma_m(g)_{i'j'} = \frac{h}{\sqrt{d_k d_m}}\delta_{km}\delta_{ii'}\delta_{jj'} \tag{15.11}$$

For most applications we do not actually need the full Great Orthogonality Theorem. A little mathematical trickery transforms Equation 15.11 into the 'Little Orthogonality Theorem' (or LOT), which is expressed in terms of the characters of the irreducible representations rather than the irreducible representations themselves.

$$\sum_g \chi_k(g)\chi_m(g) = h\delta_{km} \tag{15.12}$$

Since the characters for two symmetry operations in the same class are the same, we can also rewrite the sum over symmetry operations as a sum over classes.

$$\sum_C n_C\chi_k(C)\chi_m(C) = h\delta_{km} \tag{15.13}$$

where n_C is the number of symmetry operations in class C.

In all of the examples we've considered so far, the characters have been real. However, this is not necessarily true for all point groups, so to make the above equations completely general we need to include the possibility of imaginary characters. In this case we have:

$$\sum_C n_C\chi_k^*(C)\chi_m(C) = h\delta_{km} \tag{15.14}$$

25.a). How will you construct the character table for a C_{2v} and C_{3v} point group using the great orthogonality theorem?

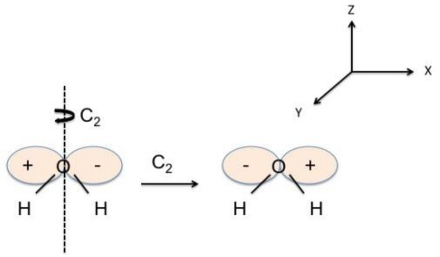
Once the point group of a molecule is known, we can begin to make use of character tables. Group theoretical considerations and matrix algebra have produced a solid mathematical foundation for the information found in character tables. However, it would be too lengthy and beyond the scope of this course to cover this material rigorously. Fortunately, it is not necessary to have a full and complete understanding of the background theory in order to be able to use character tables to solve problems related to symmetry. We will approach the material from a more descriptive view point.

What is a Character Table?

As we shall shortly discover, each point group has its own unique character table which is a device containing useful symmetry related information. A simple way of thinking about how a character table is constructed is to firstly, recognize that the positions of the atoms of a molecule (let's say water for example) conform exactly and precisely to the symmetry operations for the point group to which it belongs (C_{2v} for example). That is, the appearances of the molecule before and after a symmetry operation are identical. However, molecules have other important properties which do not behave in exactly the same way as the positions of the atoms. These properties are often referred to as molecular properties, and can include simple translations, rotations, vibrations, and even the behavior of electrons in atomic orbitals. They are also referred to as "basis vectors."

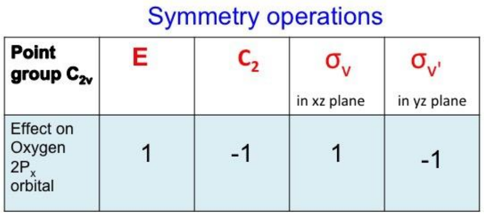
An example of how we might generate information relating to a particular molecular property is to first agree to characterize symmetric behavior at +1 and antisymmetric behavior as -1, and to call the +1's and -1's the *character* of the property with respect to the symmetry operation. For water, we place the O atom at the origin of the cartesian coordinate system and examine the behavior of the P_x orbital on O. [Note that the + and - in the figure refer to the angular dependence of the wave function.]

We now perform one of the symmetry operations for C_{2v} (ignore the positions of the O and H atoms for the moment). If we choose the C_2 operation then we would rotate the molecule about the Z axis.



Effect on oxygen $2P_x$ orbital when C_2 operation is performed.

The sign of the wave function changes and we describe this as antisymmetric behavior and give it the character -1. We can perform this analysis for all four operations for C_{2v} and tabulate the results.

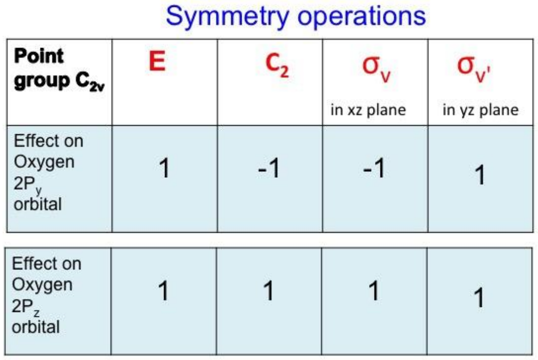


Symmetry operations

Point group C_{2v}	E	C_2	σ_v in xz plane	$\sigma_{v'}$ in yz plane
Effect on Oxygen $2P_x$ orbital	1	-1	1	-1

1 = unaffected or unchanged
-1 = changed or reversed

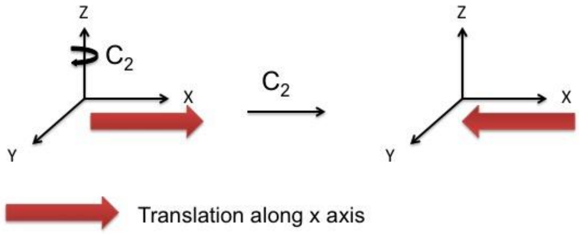
A similar treatment for the oxygen P_y and P_z orbitals gives the following table



Symmetry operations

Point group C_{2v}	E	C_2	σ_v in xz plane	$\sigma_{v'}$ in yz plane
Effect on Oxygen $2P_y$ orbital	1	-1	-1	1
Effect on Oxygen $2P_z$ orbital	1	1	1	1

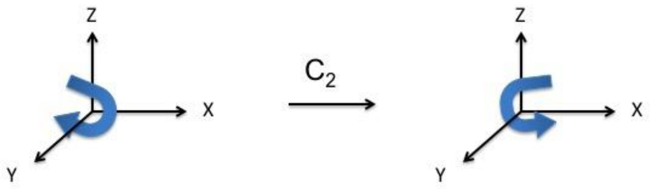
At this point we should also point out that the P orbitals lie along the x, y, and z axes, and the information that we have generated in the tables can equally be used to describe *translations* of the molecule. A translation is the movement of a molecule as a whole. T_x stands for translation along the x axis, and this can be depicted as an arrow pointing along the x direction. Performing the C_2 operation reverses the direction of the arrow and so we assign this a -1 character (just like a P_x orbital). Since we live in a 3-dimensional universe, there are three translations T_x, T_y, and T_z representing three degrees of freedom for the molecule.



Effect on translation along the x axis when C_2 operation is performed

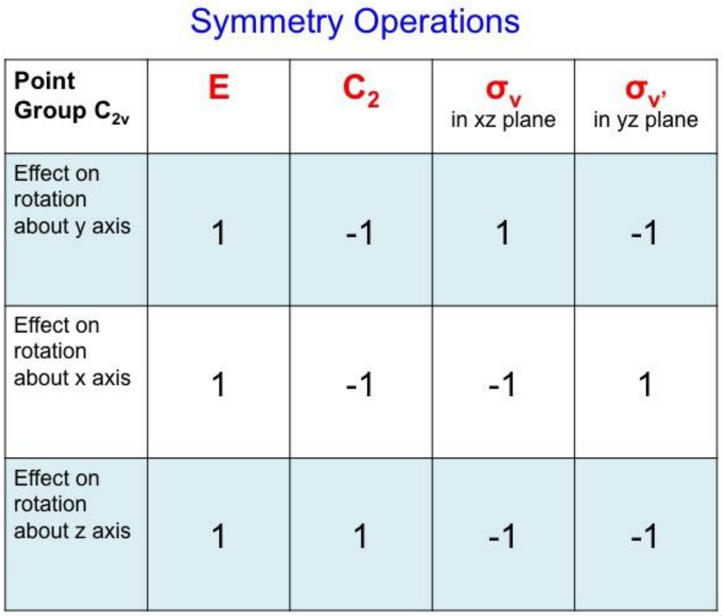
In much the same way as we treated P orbitals and translations (by "inspection") we can also consider rotations of the molecule as a whole. Again, there are three possible rotations R_x, R_y, and R_z which can be performed by rotations about the x, y, and z axes respectively. Consider the rotation R_y as if it were the steering wheel of an automobile - depicted here with a curly arrow.

After the C_2 operation, the direction of turn of the automobile has been reversed (clockwise to anticlockwise) and so we assign a -1 character.



Effect on rotation about y axis (R_y) when C_2 operation is performed

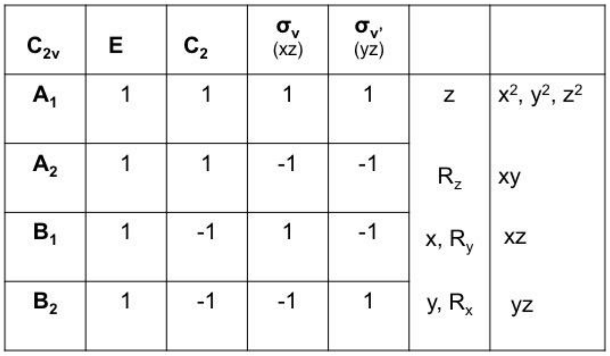
For R_y, a table of the effect on rotation about the y axis looks like this (rotations about the x and y axis have also been added)



Symmetry Operations

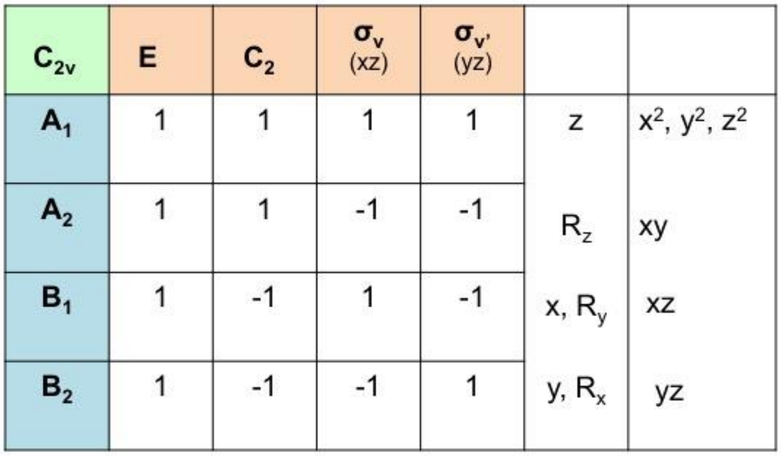
Point Group C_{2v}	**E**	**C_2**	**σ_v** in xz plane	**σ_v'** in yz plane
Effect on rotation about y axis	1	-1	1	-1
Effect on rotation about x axis	1	-1	-1	1
Effect on rotation about z axis	1	1	-1	-1

We can condense this information about the molecular properties of water into a table - a Character Table. The character table for water (C_{2v}) is shown below

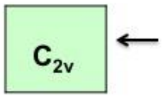


C_{2v}	E	C_2	σ_v (xz)	$\sigma_{v'}$ (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

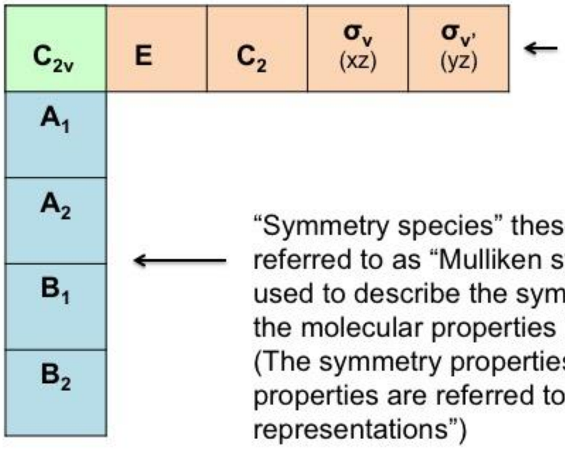
The various parts of the table can be described as follows [Note that some of this nomenclature comes from the mathematical underpinning of group theory - don't be put off by it!]



C_{2v}	E	C_2	σ_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



Point group (Schoenflies notation)



C_{2v}	E	C_2	σ_v (xz)	$\sigma_{v'}$ (yz)
A_1				
A_2				
B_1				
B_2				

Symmetry operations arranged into classes

"Symmetry species" these symbols are referred to as "Mulliken symbols" and are used to describe the symmetry properties of the molecular properties in a shorthand way. (The symmetry properties of the molecular properties are referred to a "irreducible representations")

C_{2v}	E	C_2	σ_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

The molecular properties (translations, rotations) assigned to their symmetry species. Also called "the basis functions" of the irreducible representations. You will always find 6 symbols here (x, y, z, R_x, R_y, R_z). They represent mathematical functions such as orbitals, rotations etc.

C_{2v}	**E**	**C_2**	**σ_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

A "representation" of the symmetry properties of certain molecular properties – this line is a representation of how translations in the x-direction (x) and rotations about the y axis (Ry) behave in C_{2v} point group symmetry. This is actually a mathematical code, and is found here in its simplest form - it is therefore referred to as an ***"irreducible representation"*** (Can also be referred to as "symmetry species").

C_{2v}	**E**	**C_2**	**σ_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

The "character" of an irreducible representation (symbol χ chi).

Character Tables an Example C_{3v} : (NF_3)

C_{3v}	E	C_3^1	C_3^2	σ_v	σ_v	σ_v	
	1	1	1	1	1	1	T_z
	1	1	1	-1	-1	-1	R_z
	2	-1	-1	0	0	0	(T_x, T_y) or (R_x, R_y)

This simplifies further. Some operations are of the same class and always have the same character in a given irreducible representation

C_3^1, C_3^1 are in the same **class**
$\sigma_v, \sigma_v, \sigma_v$ are in the same **class**

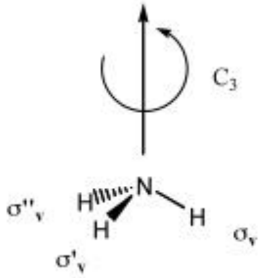
3.4. Characters and Character Tables

3.4.1. Deriving character tables: Where do all the numbers come from?

C_{3v}	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z	$x^2 + y^2, z^2$	$z^3, x(x^2 - 3y^2)$
A_2	1	1	−1	R_z		$y(3x^2 - y^2)$
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$	$(xz^2, yz^2), [xyz, z(x^2 - y^2)]$
$\Gamma_{x,y,z}$	3	0	1			

- A general and rigorous method for deriving character tables is based on five theorems which in turn are based on something called *The Great Orthogonality Theorem.* (e.g. F.A. Cotton, "Chemical Applications of Group Theory", QD 461.C65 1990)

The five theorems are:



1) The number of irreducible representations is equal to the number of classes in the group.

e.g. NH_3, point group C_{3v}:

Which C_{3v} symmetry operations are the inverse of which… and which are together in one class?

$E^{-1} = E$ $\quad \sigma_v^{-1} = \sigma_v$ $\quad C_3^{-1} = C^2_3$

$\sigma'^{-1}_v = \sigma'_v$ $\quad (C^2_3)^{-1} = C_3$ $\quad \sigma''^{-1}_v = \sigma''_v$

Using the above relationships we can set up the following similarity transformations:

$\sigma_v \text{ x } C_3 \text{ x } \sigma_v = C^2_3$

$\sigma''_v \text{ x } C_3 \text{ x } \sigma''_v = C^2_3$

$C^2_3 \text{ x } C^2_3 \text{ x } C_3 = C^2_3$

$\sigma'_v \text{ x } C^2_3 \text{ x } \sigma'_v = C_3$

$C^2_3 \text{ x } \sigma_v \text{ x } C_3 = \sigma''_v$

$\sigma_v \text{ x } \sigma_v \text{ x } \sigma_v = \sigma_v$

$C_3 \text{ x } \sigma_v \text{ x } C^2_3 = \sigma'_v$

$\sigma''_v \text{ x } \sigma'_v \text{ x } \sigma''_v = \sigma_v$

$\sigma'_v \text{ x } \sigma''_v \text{ x } \sigma'_v = \sigma_v$

$C^2_3 \text{ x } E \text{ x } C_3 = E$

$\sigma_v \text{ x } E \text{ x } \sigma_v = E$

$\sigma''_v \text{ x } E \text{ x } \sigma''_v = E$

→ Apparently $\{C_3, C^2_3\}$, $\{\sigma_v, \sigma'_v, \sigma''_v\}$, and $\{E\}$ are each in a class.

→ In C_{3v} there are three classes and hence three irreducible representations.

OR

b). Explain the symmetry selection rules for Infra-red and Raman spectra.

Selection Rules for Vibrational Spectroscopy

The fundamental modes of vibration of a molecule are active (observable) by IR or Raman spectroscopy if they meet the appropriate selection rules.

A vibration is IR active if there is a change in **dipole moment** during the vibration. Fortunately this information is also found in the character tables. Vibrations which occur with a change in dipole moment have the same symmetry properties as translations - corresponding to the x, y or z in the molecular properties column. In our example (water) for A_1 there is a z and for B_1 an x in the column - so all three vibrations are IR active and observable. We would expect to see three peaks in the IR spectrum - two with A_1 symmetry and one with B_1.

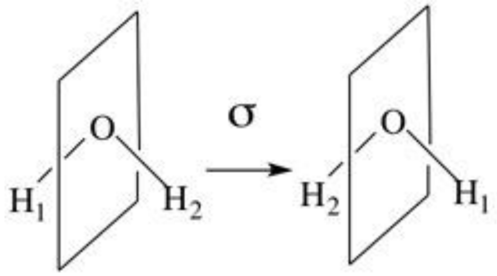
Raman spectroscopy involves inelastic light scattering and the selection rules are different from those of IR. For a vibration to be Raman active there must be a change in **polarizability** of the molecule. These vibrations correspond to symmetry species which have a product of two translations. the products are found in the far right hand column of the character table and can be simple cross products (e.g. z.y) or squares (x^2). For water all three vibrations will be Raman active.

26. a). Write a note on Elements of Symmetry?

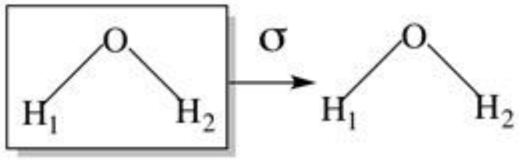
A symmetry element is a geometrical entity about which a symmetry operation is performed. A symmetry element can be a point, axis, or plane. A symmetry operation is the movement of a body (molecule) such that after the movement the molecule appears the same as before. The existence of a symmetry operation implies the existence of a corresponding symmetry element, and conversely, the presence of a symmetry element means that a certain symmetry operation or set of operations is possible.

Reflections σ and Mirror Planes

A plane of reflection in a molecule can be viewed as a double-sided mirror which bisects the molecule. It must pass through the molecule and cannot be completely outside it. The water molecule has two mirror planes, one is shown below.



This plane contains the C_2 axis and passes between the two H atoms. The effect of this σ symmetry operation is to exchange H_1 and H_2. The other mirror plane is the one which contains all three atoms of H_2O and is perpendicular to the first mirror plane show above. For this plane, H_1 and H_2 do not exchange positions. It is, nevertheless, a valid symmetry element and symmetry operation for the H_2O molecule.



The two planes of symmetry both contain the principle axis (C_2), which is designated as the vertical axis and are therefore denoted σ_v. In order to distinguish the two planes σ_v and $\sigma_v^{|}$ are often used where $\sigma_v^{|}$ contains all the atoms.

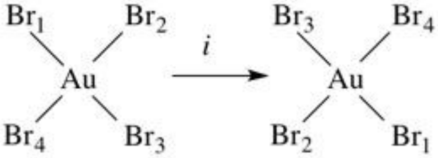
Note - the symmetry operation σ followed by another σ will result in the molecule returning to its original configuration. In other words, $\sigma^2 = E$

Inversions

Inversions (i)

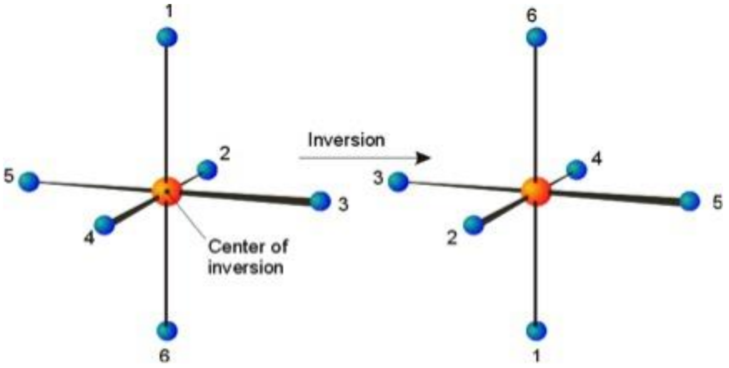
The inversion operations projects each atom through the center of inversion, and out to the same distance on the opposite side.

Note - a molecule with an inversion center can only have ***ONE*** center of inversion.
Example $[AuBr_4]^-$ This ion has a square-planar geometry about the central Au atom.



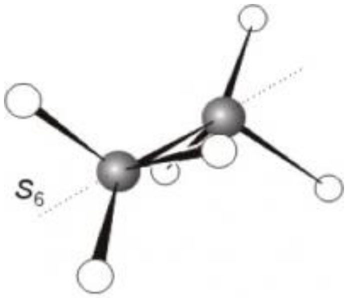
Note - the position of the Au atom does not change and as for σ, $i^2 = E$

Next Example SF_6

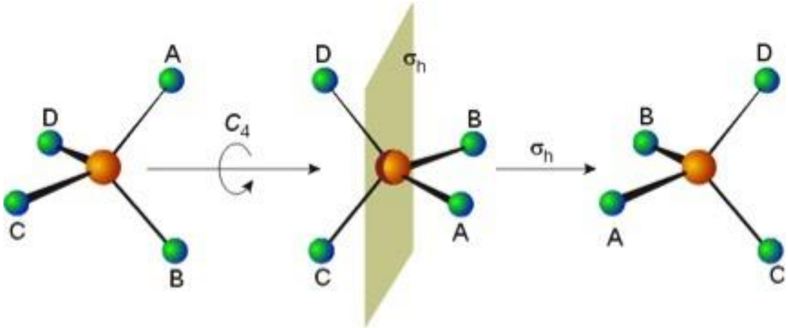


Improper Rotations S_n

An improper rotation may be thought of as two steps taken in either order. A rotation and a reflection in a plane, perpendicular to the rotation axis. This axis is referred to as an axis of improper rotation (or an improper axis) and has the symbol S_n where n denotes the order. Obviously, if an axis C_n and a perpendicular plane exist independently in a molecule then S_n exists also. However, S_n may exist when neither the C_n nor the perpendicular σ exist separately. A classic example is ethane C_2H_6 in the staggered configuration. This molecule has an S_6 axis which is coincident with a C_3 axis (running along the C-C bond). The combination of rotation and reflection always gives the same result regardless of the order in which they are performed.



Another example is that of a regular tetrahedral molecule. For example: methane (CH_4) has three C_2 axes, each of which is simultaneously an S_4 axis.

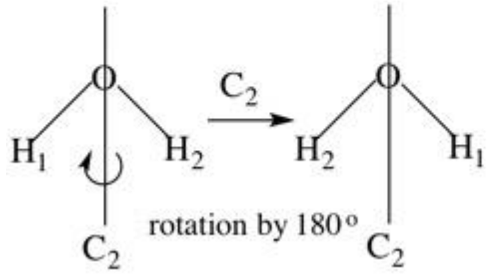


Proper Rotations - Rotation by 360°/n

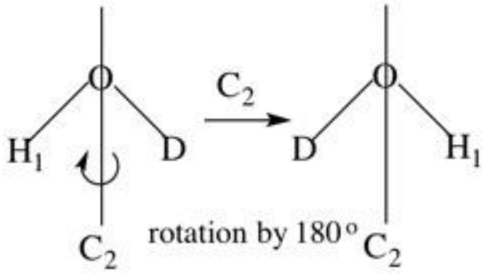
This is simply rotation about an axis, which passes through the molecule by an angle of 360°/n (or 2π/n). When repeated n times, the molecule returns to the original orientation. The appearance of the molecule must be exactly the same after the operation.

Example 1. H_2O

H_2O has a C_2 axis - rotation by 360°/2 (180°). The axis passes through O and bisects the line between the H atoms. This operation interchanges the H atoms as well as the O-H bonds. Since these atoms and bonds are equivalent, there is no detectable difference after the operation.

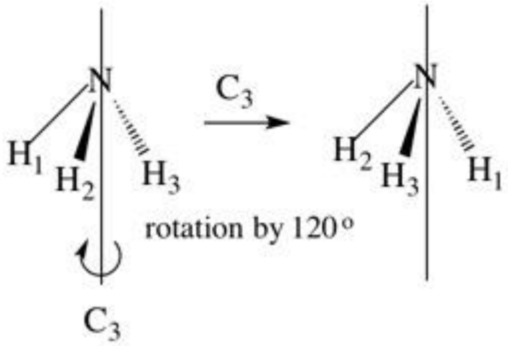


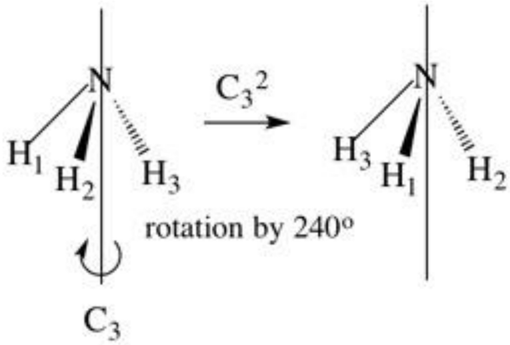
For HOD the C_2 operation results in the molecule having a different orientation. Therefore, for HOD, C_2 is **NOT** a valid symmetry operation.



Example 2. Ammonia, NH_3

This molecule has a 3-fold rotation axis (a C_3 axis) where rotation by 360°/3 (120°) produces an indistinguishable molecule (C_3). Rotation by 2 x 120° also produces a configuration which is physically indistinguishable from the original (C_3^2). Finally, rotation by 3 x 120° (360°) returns the molecule to its initial position (C_3^3). This is equivalent to performing no operation at all, and we can say that $C_3^3 = E$ where E is the identity operation. We include E for mathematical reasons. There are therefore two symmetry operations associated with the C_3 axis (C_3 and C_3^2).

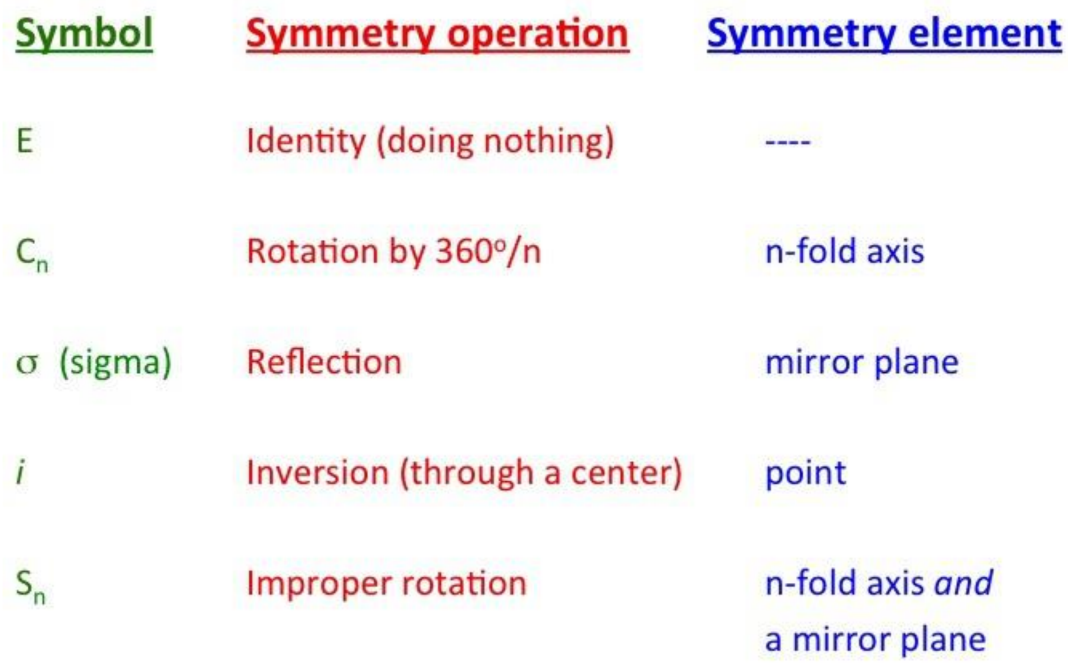




When only a single rotation axis is present, it is assigned to the Z axis by convention. If more than one rotation axis exists, the C_n of highest order (highest value of n) is assigned as the Z axis.

Note - the proper rotation operation (C_n) is the **ONLY** operation we can actually perform on either a real molecule or its macroscopic model. The remaining operations (σ, i, S_n) are non-feasible and we have to use our imaginations a little to see how they work - they have to be *visualized*.

There are five basic kinds of symmetry operations



Symbol	Symmetry operation	Symmetry element
E	Identity (doing nothing)	----
C_n	Rotation by 360°/n	n-fold axis
σ (sigma)	Reflection	mirror plane
i	Inversion (through a center)	point
S_n	Improper rotation	n-fold axis *and* a mirror plane

OR

b). Explain the great orthogonality theory and its consequences.

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,

$$\Sigma_R\ [\Gamma_i(R)_{mn}]\ [\Gamma_j(R)'_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}}\ \delta_{ij}\ \delta_{mm'}\ \delta_{nn'}$$

Where,

i, j – Irreducible Representations

l_i, l_j – Its dimensions

h – Order of a group

$\Gamma_i(R)_{mn}$ – Element of mth row, nth column of an ith 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 $\delta_{ij} = 0$

   Therefore, $\Sigma_R\ [\ \Gamma_i(R)_{mn}\ ]\ [\ \Gamma_j(R)'m'n'\ ]^* = 0$

2. When, $\Gamma_i = \Gamma_j$ and $j = i$, then $\delta_{ij} = 1$

   Therefore, $\Sigma_R\ [\ \Gamma_i(R)_{mn}\ ]\ [\ \Gamma_i(R)'m'n'\ ]^* = 0$

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 $i = j$, $m = m'$, $n = n'$

   Then, $\Sigma_R\ [\ \Gamma_i(R)_{mn}\ ]\ [\ \Gamma_i(R)\ mn]^* = \frac{h}{l_i}$

From the above equations some important rules of the irreducible representations of a group and there character were obtained.

Five Rules Obtained:

1. The sum of the squares of the dimensions of the representation = the order (h) of the group.

   i.e., $\Sigma_{li}^2 = l_1^2 + l_2^2 + l_3^2 + \ldots\ldots\ l_n^2 = h$

   $\Gamma_i(E)$ –the character of the representation of E in the ith IR which is equal to the dimension of the representation.

   i.e., $\Sigma_i\ [\ \Gamma_i(E)]^2 = h$

2. The sum of the squares of the characters in any IR is equal to 'h'.

   i.e., $\Sigma_R\ [\ \Gamma_i(R)]^2 = h$

3. The vectors whose components are the characters of two different IR are orthogonal.

i.e., $\Sigma_R \Gamma_i(R) \Gamma_j(R) = 0$ when $i \neq j$.

4. In a given representation (reducible/irreducible) the characters of all matrices belonging to operations in the same class are identical.

Eg:- in C_{3v} point group there are, E, $2C_3$, 3 σ_v. there characters are same for a particular IR.

5. No: of irreducible representation in a group = No: of classes in a group.

Applications:

Applying these 5 rules we can develop the character table for various point groups. For most chemical applications, it is sufficient to know only the characters of the each of the symmetry classes of a group.

Steps for The Construction of A Character Table::

1. Write down all the symmetry operations of the point group and group them into classes.
2. Note that the no: of the IR is found out using the theorem.
3. Interrelationships of various group operations are to be carefully followed.
4. Use the orthogonality and the normality theorem in fixing the characters.
5. Generate a representation using certain basic vectors. Try out with X, Y, Z, R_σ, R_y, R_z etc. as the bases and check.