Quick Revision

EXAM MAPPING

NTA CSIR-UGC NET CHEMICAL SCIENCE

3000+ EXAM POINTERS

COVERED COMPLETE SYLLABUS

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P R E F A C E

The **CSIR JRF/NET exam for Chemical Science** stands as a significant gateway for aspiring researchers and educators in India. It demands not just a superficial understanding but a comprehensive mastery of a vast and intricate syllabus. Recognizing the unique challenges faced by students preparing for this highly competitive examination, we are proud to present **"Exam Mapping for CSIR NET Chemical Science,"** a meticulously crafted resource designed to streamline your revision and significantly enhance your chances of success.

This book is born from the understanding that effective exam preparation requires targeted and efficient revision. Unlike conventional textbooks that offer detailed narratives, **"Exam Mapping for CSIR NET Chemical Science"** adopts a unique pointer-based approach. We have painstakingly distilled all the key concepts from the CSIR NET Chemical Science syllabus—namely, **Inorganic Chemistry, Physical Chemistry, and Organic Chemistry**—into exam-relevant pointers.

This structure makes the book an unparalleled tool for **rapid revision**. Imagine being able to scan through the most crucial information for each topic quickly, reinforce your memory of essential facts, and identify areas that require further attention—all within a fraction of the time it would take to reread traditional texts. Each pointer is designed to be a direct hit on frequently tested concepts, ensuring that your study time is optimized for maximum impact.

We aim to provide a comprehensive yet compact guide that empowers you to consolidate your knowledge, identify critical interconnections between different branches of chemistry, and recall information with precision during the examination. We have meticulously analyzed past CSIR NET papers to ensure that the content aligns perfectly with the exam's demands, covering both fundamental principles and frequently appearing advanced concepts.

This book is more than just a collection of facts; it is a strategic study aid that will guide you through the complexities of the syllabus, allowing you to build confidence and develop a strong command over the subject matter. We are confident that by leveraging this resource, you will not only gain a deeper understanding of chemical sciences but also develop the strategic edge necessary to excel in the CSIR NET examination. Your dedication, combined with the focused approach offered by this book, will undoubtedly increase your chances of selection and pave the way for a successful career in scientific research and academia.

We wish you the very best in your preparations and your pursuit of excellence.

CSIR-UGC NET Cutoff for Junior Research Fellowship (JRF))

YEAR	UR (%)	EWS (%)	OBC (%)	SC (%)	ST (%)	PwD (%)
JUNE 2025	50.75	44.50	43.75	33.25	28.00	25.50
JULY 2024	55.500	47.500	47.750	36.000	30.750	25.000
DEC 2023	59.00	51.50	51.00	39.25	30.50	25.00
JUNE 2023	53.75	48.25	47.25	37.25	30.75	25.00
SEP 2022	50.75	44.25	43.50	33.50	27.50	25.00
FEB 2022	52.75	46.25	45.50	36.25	27.25	25.00
NOV 2020	50.50	44.50	43.25	33.25	25.50	25.50
DEC 2019	55.25	50.50	47.50	39.75	29.50	25.00
JUNE 2019	47.75	36.25	41.75	34.25	28.00	25.00
DEC 2018	57.75	-	49.75	40.25	30.25	26.00
JUNE 2018	48.00	-	41.00	33.50	25.25	25.00

CSIR-UGC NET Cutoff for Lectureship (LS)

YEAR	UR (%)	EWS (%)	OBC (%)	SC (%)	ST (%)	PwD (%)
JUNE 2025	50.75	45.675	40.05	39.375	29.925	25.000
JULY 2024	49.950	42.750	42.975	32.400	27.675	25.000
DEC 2023	53.10	46.35	45.90	35.325	27.45	25.00
JUNE 2023	48.375	43.425	42.525	33.525	27.675	25.00
SEP 2022	45.675	39.825	39.150	30.150	25.00	25.00
FEB 2022	47.48	41.63	40.95	32.63	25.00	25.00
NOV 2020	45.45	40.05	38.92	29.92	25.00	25.00
DEC 2019	49.73	49.73	42.75	35.78	26.55	25.00
JUNE 2019	42.98	33.00	37.58	30.83	25.20	25.00
DEC 2018	51.98	-	44.78	36.23	27.23	25.00
JUNE 2018	43.20	-	36.90	30.15	25.00	25.00

Aim and Scheme of Examination

The Council of Scientific and Industrial Research (CSIR) has entrusted the responsibility of conducting CSIR-UGC NET in **CBT mode** to NTA. **CSIR-UGC NET** is a test being conducted to determine the eligibility for Junior Research Fellowship (JRF) and for Lectureship/Assistant Professor in Indian universities and colleges subject to fulfilling the eligibility criteria laid down by UGC. Online applications for JRF/NET are invited twice a year on all India basis through Press Notification of CSIR-UGC NET for JRF and LS/AP CSIR and UGC provide Research Fellowships for training in methods of research under expert guidance of faculty members/scientists working in University Department/ National Laboratories and institutions in various fields of Science. CSIR-UGC NET Fellowships are tenable in Universities/IITs/Post Graduate Colleges/Govt. Research Establishments including those of the CSIR, Research Development establishments of recognized public or private sector industrial firms and other recognized institutions. Only bonafide Indian Citizens are eligible for the test. CSIR-UGC NET Fellowship is tenable in India. The programme is aimed at National Science & Technology Human Resource Development.

The pattern for the Single Paper **MCQ** test shall be as given below:

- The MCQ test paper of each subject shall carry a maximum of 200 marks.
- The exam shall be for duration of three hours.
- The question paper shall be divided in three parts

Part 'A' shall be common to all subjects. This part shall be a test containing a maximum of **20 questions** of General Aptitude. The candidates shall be required to answer any **15 questions** of two marks each. The total marks allocated to this section shall be 30 out of 200.

Part 'B' shall contain subject-related **40 conventional MCQs**, each of two marks. The candidates shall be required to answer any **35 questions** of two marks each. The total marks allocated to this section shall be 70 out of 200.

Part 'C' shall contain **60 higher value questions** that may test the candidate's knowledge of scientific concepts and/or application of the scientific concepts. The questions shall be of analytical nature where a candidate is expected to apply the scientific knowledge to arrive at the solution to the given scientific problem. The candidates shall be required to answer any **25 questions** of four marks each. The total marks allocated to this section shall be 100 out of 200.

Negative marking for wrong answers will be **@ 1/4** for all three sections.

CSIR-UGC National Eligibility Test (NET) for Junior Research Fellowship and Lecturer-ship

CHEMICAL SCIENCES

Inorganic Chemistry

1. Chemical periodicity
2. Structure and bonding in homo- and heteronuclear molecules, including shapes of molecules (VSEPR Theory).
3. Concepts of acids and bases, Hard-Soft acid base concept, Non-aqueous solvents.
4. Main group elements and their compounds: Allotropy, synthesis, structure and bonding, industrial importance of the compounds.
5. Transition elements and coordination compounds: structure, bonding theories, spectral and magnetic properties, reaction mechanisms.
6. Inner transition elements: spectral and magnetic properties, redox chemistry, analytical applications.
7. Organometallic compounds: synthesis, bonding and structure, and reactivity. Organometallics in homogeneous catalysis.
8. Cages and metal clusters.
9. Analytical chemistry- separation, spectroscopic, electro- and thermoanalytical methods.
10. Bioinorganic chemistry: photosystems, porphyrins, metalloenzymes, oxygen transport, electron-transfer reactions; nitrogen fixation, metal complexes in medicine.
11. Characterisation of inorganic compounds by IR, Raman, NMR, EPR, Mössbauer, UV-vis, NQR, MS, electron spectroscopy and microscopic techniques.
12. Nuclear chemistry: nuclear reactions, fission and fusion, radio-analytical techniques and activation analysis.

Physical Chemistry:

1. Basic principles of quantum mechanics: Postulates; operator algebra; exactlysolvable systems: particle-in-a-box, harmonic oscillator and the hydrogen atom, including shapes of atomic orbitals; orbital and spin angular momenta; tunneling.
2. Approximate methods of quantum mechanics: Variational principle; perturbation theory up to second order in energy; applications.
3. Atomic structure and spectroscopy; term symbols; many-electron systems and antisymmetry principle.
4. Chemical bonding in diatomics; elementary concepts of MO and VB theories; Huckel theory for conjugated π-electron systems.
5. Chemical applications of group theory; symmetry elements; point groups; character tables; selection rules.
6. Molecular spectroscopy: Rotational and vibrational spectra of diatomic molecules; electronic spectra; IR and Raman activities - selection rules; basic principles of magnetic resonance.

7. Chemical thermodynamics: Laws, state and path functions and their applications; thermodynamic description of various types of processes; Maxwell's relations; spontaneity and equilibria; temperature and pressure dependence of thermodynamic quantities; Le Chatelier principle; elementary description of phase transitions; phase equilibria and phase rule; thermodynamics of ideal and non-ideal gases, and solutions.
8. Statistical thermodynamics: Boltzmann distribution; kinetic theory of gases; partition functions and their relation to thermodynamic quantities - calculations for model systems.
9. Electrochemistry: Nernst equation, redox systems, electrochemical cells; DebyeHuckel theory; electrolytic conductance-Kohlrausch's law and its applications; ionic equilibria; conductometric and potentiometric titrations.
10. Chemical kinetics: Empirical rate laws and temperature dependence; complex reactions; steady state approximation; determination of reaction mechanisms; collision and transition state theories of rate constants; unimolecular reactions; enzyme kinetics; salt effects; homogeneous catalysis; photochemical reactions.
11. Colloids and surfaces: Stability and properties of colloids; isotherms and surface area; heterogeneous catalysis.
12. Solid state: Crystal structures; Bragg's law and applications; band structure of solids.
13. Polymer chemistry: Molar masses; kinetics of polymerization.
14. Data analysis: Mean and standard deviation; absolute and relative errors; linear regression; covariance and correlation coefficient.

Organic Chemistry

1. IUPAC nomenclature of organic molecules including regio- and stereoisomers.
2. Principles of stereochemistry: Configurational and conformational isomerism in acyclic and cyclic compounds; stereogenicity, stereoselectivity, enantioselectivity, diastereoselectivity and asymmetric induction.
3. Aromaticity: Benzenoid and non-benzenoid compounds - generation and reactions.
4. Organic reactive intermediates: Generation, stability and reactivity of carbocations, carbanions, free radicals, carbenes, benzynes and nitrenes.
5. Organic reaction mechanisms involving addition, elimination and substitution reactions with electrophilic, nucleophilic or radical species. Determination of reaction pathways.
6. Common named reactions and rearrangements - applications in organic synthesis.
7. Organic transformations and reagents: Functional group interconversion including oxidations and reductions; common catalysts and reagents (organic, inorganic, organometallic and enzymatic). Chemo, regio and stereoselective transformations.
8. Concepts in organic synthesis: Retrosynthesis, disconnection, synthons, linear and convergent synthesis, umpolung of reactivity and protecting groups.

9. Asymmetric synthesis: Chiral auxiliaries, methods of asymmetric induction substrate, reagent and catalyst controlled reactions; determination of enantiomeric and diastereomeric excess; enantio-discrimination. Resolution - optical and kinetic.
10. Pericyclic reactions - electrocyclisation, cycloaddition, sigmatropic rearrangements and other related concerted reactions. Principles and applications of photochemical reactions in organic chemistry.
11. Synthesis and reactivity of common heterocyclic compounds containing one or two heteroatoms (O, N, S).
12. Chemistry of natural products: Carbohydrates, proteins and peptides, fatty acids, nucleic acids, terpenes, steroids and alkaloids. Biogenesis of terpenoids and alkaloids.
13. Structure determination of organic compounds by IR, UV-Vis, ^{1}H & ^{13}C NMR and Mass spectroscopic techniques.

Interdisciplinary topics

1. Chemistry in nanoscience and technology.
2. Catalysis and green chemistry.
3. Medicinal chemistry.
4. Supramolecular chemistry.
5. Environmental chemistry.

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SECTION - I

"INORGANIC CHEMISTRY"

CHAPTER - 1

CHEMICAL PERIODICITY

The principal Quantum Number 'n'

It is a positive integer with value of n = 1,2,3..... The principal quantum number determines the size and to large extent the energy of the orbital. Size of an orbital increases with increase of principal quantum number 'n'.

Azimuthal Quantum Number. 'l'

It is also known as orbital angular momentum or subsidiary quantum number. It defines the three-dimensional shape of the orbital.

Magnetic Quantum Number (m_l)

i. The electrons in a given energy sublevel can orient themselves in certain specific regions of space around the nucleus. These regions of space are called 'orbital's'.
ii. The number of orbital's in a given energy sublevel within a principal energy level is given by the 'Magnetic Quantum number' (m_l).
iii. The possible value of ml ranges from - l through 0 to + l. Thus, making a total of 2l + 1 values. Each sub shell can have (2l + 1) degenerate orbitals.

The Magnetic Momentum:

An electron in orbit around the nucleus of an atom can be seen as tiny of current I, generating an Orbital Magnetic Moment, $\mu_l = \sqrt{l(l+1)}\,\mu B$

The spin only angular momentum is given by:

$\mu_s = \sqrt{s(s+2)}\,\mu B$

Nodes and their types:

The point, where the probability of finding an electron at the surface is zero is called 'node'. The node can be a point referred to as node or a surface referred to as nodal plane.

Radial nodes

i. Radial Node for any orbital is given by the equation (n - l - 1)

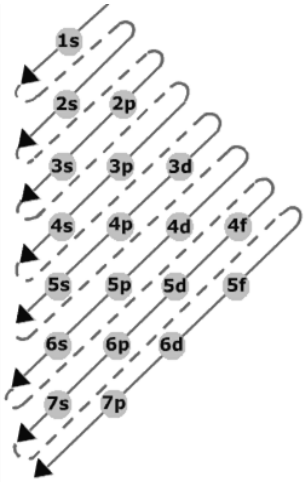
Angular nodes

i. Angular Node for any orbital is given by the equation (l)
ii. For any s – orbital, the number of angular node is equal to 0
iii. For any p – orbital, the number of angular node is equal to 1
iv. For any d – orbital, the number of angular node is equal to 2

Filling of Orbital's in Atom:

The filling of electrons into the orbital's of different atoms takes place according to the Aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

Aufbau Principle:



Pauli Exclusion Principle

According to this principle: No two electrons in an atom can have the same set of four quantum numbers. Pauli exclusion principle can also be stated as: "Only two electrons may exist in the same orbital and these electrons must have opposite spin." This means that the two electrons can have the same value of three quantum numbers n, l and ml, but must have the opposite spin quantum number.

Hund's Rule of Maximum Multiplicity

This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called degenerate orbitals). It states: pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.

Melting and boiling points:

i. Following figure shows the variation of melting and boiling points of the elements with atomic number 1–95; elements can be identified with reference to the periodic table.

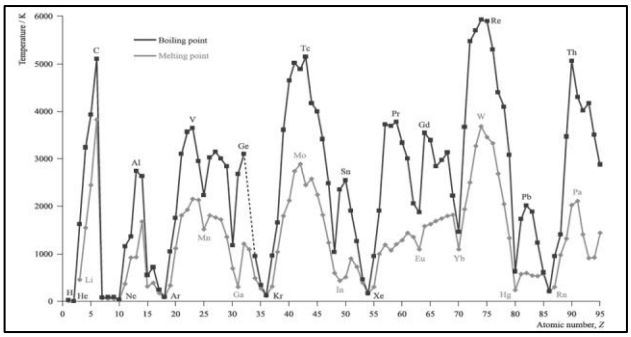


Fig 1.8: Variation of MP and BP of elements from atomic number 1-95

ii. Some points to note from Figure are:

a) The extremely low values of melting and boiling points of hydrogen;

b) The very low melting and boiling points of the group 18 elements (the noble gases);

c) The relatively short liquid ranges of H, He, N, O, F, Ne, Cl, Ar, Kr, Xe and Rn, i.e. the elements that are gases at 298 K;

d) The extremely high melting and boiling points of carbon;

e) The sharp drop in boiling point after each group 14 element, C, Si, Ge, Sn;

f) The similar trends across the three rows of d-block elements, Z= 21–30, 39–48 and 72–80, and the low melting points of the last (group 12) metal of each row of the d-block;

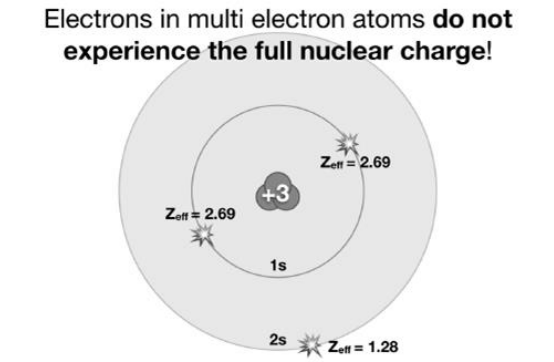
g) The roughly repeating patterns of the melting and boiling points of the s-, p- and d-block elements, and the insertion of the first row of the f-block metals (Z =57–71) at the beginning of the third row of the d-block;

h) The high melting points of metals in the middle of the third row of the d-block metals;

i) The rather similar melting points of the first-row f-block metals.

PERIODICITY IN PROPERTIES:

EFFECTIVE NUCLEUR CHARGE (Z_{eff})



Effective nuclear charge (Z_{eff}) is the charge that each electron experiences.

Slater's rules:

Effective nuclear charges, Zeff, experienced by electrons in different atomic orbitals may be estimated using Slater's rules. These rules are based on experimental data for electron promotion and ionization energies, and Zeff is determined from the equation: Zeff = Z – σ.

For ns or np orbital electrons: Electron in any group higher in this sequence than the electron under consideration contribute nothing to σ. All other electrons in the same (ns, np) group contribute 0.35 each (except for 1s the value of σ is 0.30). All the electrons in the (n-1) shell contribute 0.85 each. All the electron in (n-2) or lower shell contributes 1.00 each.

For d or f-electrons:

All the electrons in the same group contribute 0.35 each. All the electrons in the groups lying left of this group contribute1.00 each.

Trends

The periodic table tendency for effective nuclear charge:

- Increase across a period (due to increasing nuclear charge with no accompanying increase in shielding effect).
- Decrease down a group (although nuclear charge increases down a group, shielding effect more than counters its effect).

Note: When screening effect decrease the effective nuclear charge increase. The effective nuclear charge increases with increasing charge of the nucleus (increase No. of protons), decreasing shielding effect.

Effective nuclear charge Z* increases very slowly down a group for the "valence" i.e. outermost orbital.

Atomic Size

Atomic size is the distance between the center of the nucleus of an atom and its outermost shell.

Factors affecting atomic size

1) Principal quantum number increases (n) atomic size increases.
2) Z_{eff} increase, size decreases.

Atomic Radii

Atomic radius is generally stated as being the total distance from an atom's nucleus to the outermost orbital of electron.

Types of Atomic Radius

Based on the type of bond, atomic radius is divided into Four types as follows:

- Covalent Radius
- Ionic Radius
- Metallic Radius
- Van Der Waals Radius

Covalent Radius

The covalent radius of an atom is the radius of an atom under the covalent bond with another atom(s) of a similar element

Ionic Radius

The ionic radius is the radius of an atom forming an ionic bond or an ion. The atomic bonds restrict the electrons and nucleus, and due to this, the ions or atoms don't have a specific shape.

Metallic Radius

The metallic radius is the radius of an atom joined by the metallic bond. The metallic radius is half of the total distance between the nuclei of two adjacent atoms in a metallic cluster.

Van-der-Waals radii:-

Van-der-Waals radii are determined from the contact distances between unbonded atoms in touching molecules or atoms.

Ionization Energy

Ionization energy as the minimum energy that an electron in a gaseous atom or ion has to absorb to come out of the influence of the nucleus.

Factors Governing Ionization Energy

- If the nucleus is positively charged then the electrons are strongly attracted to it.
- If an electron lies near or close to the nucleus then the attraction will be greater than the one when the electron is further away.
- If there are more electrons between the outer level and the nucleus the attraction forces are less.
- When there are two electrons in the same orbital they experience some form of repulsion. Now, this creates disturbances in the attraction of the nucleus. In essence, ionization energy will be less in paired electrons as they can be removed easily

FACTOR AFFECTING I.E:

(1) Size of Atom: The ionization energy decreases with increase in atomic size and increases with decrease in atomic size. As the size increases the outer most electrons lie farther away from the nucleus, hence the IP potential decreases (Li-Na-k-Rb-Cs) IE ∝ 1/Size

(2) Effective Nuclear Charge: (Zeff) Atomic size decreases with increases in effective nuclear charge because, higher the effective nuclear charge stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the I.E. IE ∝ Zeff

(3) Penetration Power: In any atom, the s orbital is nearer to the nucleus in comparision to p, d, and f orbitals. Therefore, greater energy is required to remove an electron from s orbital than from p, d and f orbitals. Thus the decreasing order of ionization potential of s, p, d and f orbitals is as follows: s > p > d > f

(4) Shielding effect: An increase in shielding effect, decreases the nuclear charge. This result in decrease of I.E IE ∝ 1/ Shielding effect.

(5) Stability of half filled and fully filled orbitals: The atoms whose orbitals are half filled (p3 , d 5 ,f7) or fully filled (p6 , d10, f14) have greater stability than the others. Therefore, they require greater amount of energy for removing an electron. However, stability of fully filled orbitals is greater than that of the half filled orbitals.

Important Points:

1. In the periodic table the element having highest value of I.E is He.
2. The value of I.E of noble gases are extremely high, because the outermost orbitals are fully filled (ns2 , np6) and provide great stability.
3. In a period, the elements having least value of I.E are alkali metals (group 1) and those having highest value are inert gas (group 18).

Application of ionization energy:

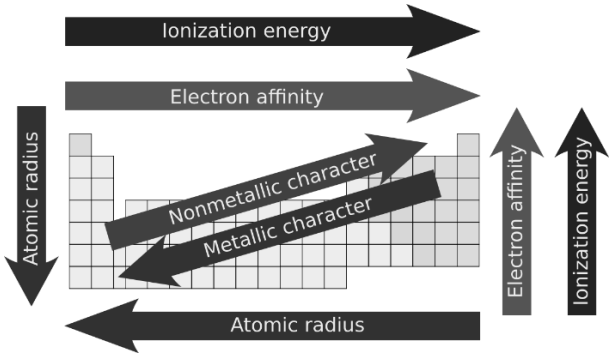
1. Metallic and non metallic characters The elements having low value of ionization energy readily lose electron and thus exhibit greater metallic property.
2. Reactivity ∞ 1/ IE Reactivity of metals is controlled by their I.E while reactivity of non metals (Halogens) is controlled by their electronegativity. So, halogens are highly reactive because of their higher electronegativity.
3. Basic Property The elements having low value of Ionization energy readily lose electron and thus oxide and hydroxide of these elements have basic property.
4. Reducing Nature: The element having low value of ionization energy behave as strong reducing agent. Reducing Power ∞ 1/ Ionization Energy. For example Alkali Metals: Here solvation energy of Li is greater than Cs, so the reducing power is greater than Cs. Li > Cs > Rb > K > Na but, in gaseous phase - Cs > Rb > K > Na > Li, because in gaseous phase solvation energy is absent.

Electronegativity

The tendency of an atom in a molecule to attract the shared pair of electrons towards itself is known as **electronegativity**.

Factors Affecting Electronegativity

1. **Size of an Atom:**
   A greater atomic size will result in less value of electronegativity.
2. **Nuclear Charge:**
   A greater value of nuclear charge will result in a greater value of electronegativity.
3. **Effect of Substituent:**
   The electronegativity of an atom depends upon the nature of the substituent attached to that atom. For example, the carbon atom in CF_3I acquires a greater positive charge than CH_3I. Therefore, C-atom in CF_3I is more electronegative than in CH_3I.



Electron Affinity:

The amount of energy released when an electron is added to a neutral atom to form an anion.

The melting and boiling points of the Group 1 elements decrease on descending the group.

- ***Electron affinity increases going left to right across a period*** because of increased nuclear attraction.
- ***Going down the group the electron affinity should decrease*** since the electron is being added increasingly further away from the nucleus. Electron becomes less tightly bound and can be easily removed

$$electron\ affinity \propto \frac{1}{atomic\ size}$$

Factors Affecting Electron Affinity

The general factors that affect electron affinity are listed below.

1. $electron\ affinity \propto \frac{1}{atomic\ size}$
2. $electron\ affinity \propto effective\ nuclear\ charge$
3. $electron\ affinity \propto \frac{1}{screening\ effect}$

Important points:

1. Electron affinity order: S > Se > Te > Po > O
2. Cl > F > Br > I

Electro positivity OR Metallic Property:

Electro positivity can be defined as the tendency of an atom to donate electrons to form positively charged cations. The property to form positively charged cations is most probably exhibited by the metallic elements in the periodic table, especially the alkali metals and the alkaline earth metals.

Top 5 Electropositive Elements

The most selective feature in the timeline is Cesium (Cs). A list of the top five energy selection items is given below:

(1) Caesium
(2) Rubidium
(3) Potassium
(4) Sodium
(5) Lithium

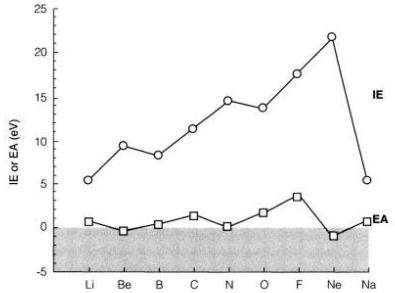


Fig. 1. Ionization energies (IE) and electron affinities (EA) for the elements Li-Na.

Diagonal Relationship:

A diagonal relationship in S-block elements exists between adjacent elements which are located in the second and third period of the periodic table.

Group			
IA	IIA	IIIA	IVA
Li	Be	B	C
Na	Mg	Al	Si

Diagonal elements possess similar properties like density, atomic size, electronegativity, polarizing power and chemical properties.

ACID BASE CHARACTER OF OXIDE

On moving across a period, the basic character of the oxides gradually changes first into amphoteric and finally into acidic character. On moving down the group, reverse behaviour is observed, i.e., from more acidic to more basic.

Stability of oxides decreases across a period.

Basicity order:

$$Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$$

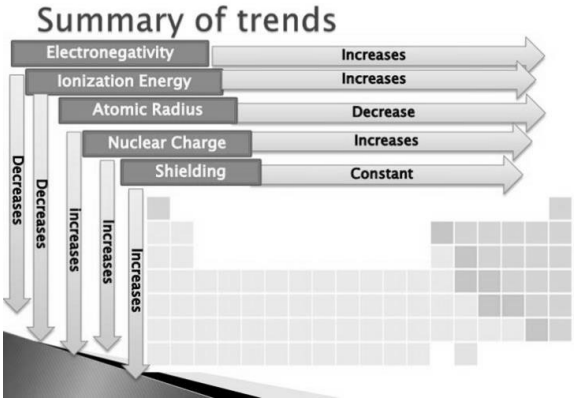
Basicity order:

$$MgO > Al_2O_3 > SiO_2 > P_2O_5 > SO_3 > Cl_2O_7$$

Oxides of the following elements are amphoteric

H , Be , Al , Ga , In , Tl , Sn , Pb , Sb , Bi , Zn , As , Ge

H_2O is amphoteric (also called amphiprotic)



SECTION - II

"PHYSICAL CHEMISTRY"

C H A P T E R - 1

QUANTUM CHEMISTRY

Huygens Principle:

Huygens' Wave Theory: Postulates on which Huygens' wave theory are given as follows:

1. The source of light emits light in the form of waves.
2. Light waves are like sound wave, which are longitudinal in nature.
3. Light waves move with constant speed in a homogeneous medium.
4. Different colours of light are due to different wavelengths of light waves.
5. When light waves enter in our eyes we feel the sensation of vision.
6. Light waves travel through vacuum due to presence of a hypothetical medium called as luminiferous ether.

Merits:

1. Wave theory of light is helpful to explain phenomena such as reflection, refraction, interference and diffraction.
2. The phenomenon of Partial reflection and refraction of light can be satisfactorily explained using the wave theory of light.
3. As per the wave theory of light, velocity of light in optically denser medium is less than the velocity of light in a rarer medium, which is correct ($va>vd$).

Demerits:

1. Wave theory of light assumed the presence of hypothetical ether medium but experiment proved that there is no ether or drag.
2. Rectilinear propagation of light is not explained by this wave theory.
3. Wave theory of light could not explain phenomena such as Compton effect and polarization of light.
4. Wave theory of light could not explain bending of wave through an obstacle.
5. Wave theory of light assumed that light waves are longitudinal in nature but experiment proved that they are electromagnetic transverse waves.

Blackbody Radiation

- Stefan-Boltzmann law: The total intensity of blackbody radiation emitted by an object (obtained by integrating the curves in Figure 1 over all wavelengths) is proportional to the fourth power of the absolute temperature (that is, the temperature in kelvins)
  (total radiant emittance) = $\boldsymbol{\sigma T^4}$
  Wien's Law: The wavelength of maximum intensity ($\lambda_{\max}$) is inversely proportional to the absolute temperature:
  $\lambda_{\max} T = 2.90\ x\ 10^{-3} m.K$

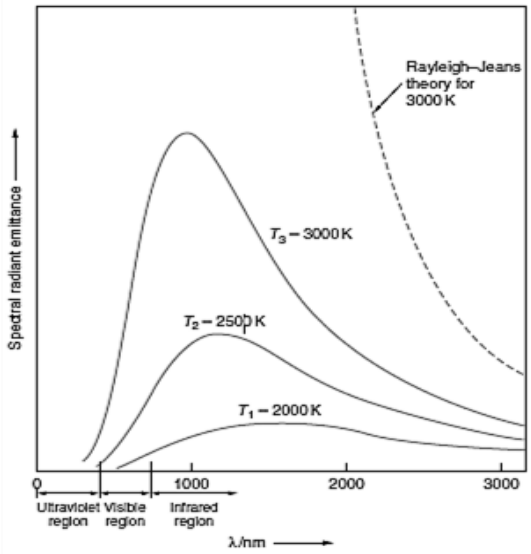


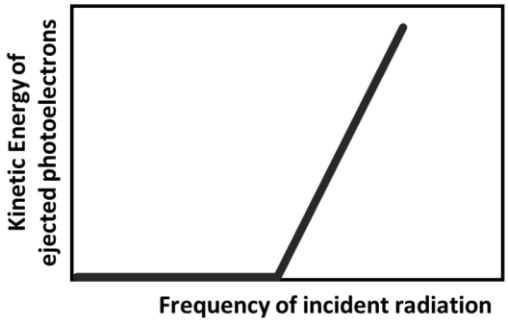
Figure. The Quantized Energies of an Oscillator as Postulated by Planck.
The horizontal line segments are plotted at the heights of the assumed energy values, 0, hv, 2hv, 3hv, 4hv, 5hv, 6hv, 7hv, etc.

Einstein's Theory of the Photoelectric Effect:

The photoelectric effect is characterized by three primary observations:

- The number of electrons ejected is proportional to the intensity of the light.

- No electrons can be ejected if the frequency of the light is lower than a certain threshold frequency, which depends upon the identity of the metal.
- The kinetic energy of the ejected electrons is proportional to the difference between the frequency of the incident light and the threshold frequency.



Kinetic energy of ejected electrons versus the frequency of applied electromagnetic radiation.

The photoelectric effect could not be explained by the wave theory of light. In the wave theory the energy of a light wave is proportional to the square of the amplitude (intensity) of the light wave, not its frequency. This contradicts the second observation of the photoelectric effect. Building on Planck's hypothesis, Einstein was able to explain the photoelectric effect by assuming that light consisted of particles (light quanta) of energy hν, where ν is the frequency of the light. These particles of light are called **photons.**

The Wave–Particle Duality of Light:

Since light exhibits a particle-like nature in some experiments and wave-like properties in other experiments, we say that it exhibits a wave–particle duality. We cannot give a simple answer to the question: "What is light really like?" We use the wave description when it explains a particular experiment, and use the particle description when it explains another experiments like interference, diffraction, etc.

The Bohr Model Was an Early Attempt to Formulate a Quantum Theory of Matter:

The work of Planck and Einstein showed that the energy of electromagnetic radiation at a given frequency (ν) is quantized in units of h ν. The extension of this quantum hypothesis to matter paved the way for the solution of yet another nineteenth-century mystery in physics: the emission spectra of atoms.

The Emission Spectrum of Hydrogen:

$$\bar{\nu} or \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 109680\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^{-1} \quad and\ (n_2 > n_1)$$

The First Five Spectral Series in the Emission Spectrum of Hydrogen

Series	n_1	n_2	**Spectral Region**
Lyman	1	2, 3, 4, …..	Ultraviolet
Balmer	2	3, 4, 5, …..	Visible
Paschen	3	4, 5, 6 ,……	Near Infrared
Bracket	4	5, 6, 7,……	Infrared
Pfund	5	6, 7, 8 ,……	Far infrared

The Wave-Particle Duality of Matter—The de Broglie Hypothesis:

$$E = \frac{hc}{\lambda} = pc\ or\ \lambda = \frac{h}{p}$$

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

In terms of kinetic energy

$$p = \sqrt{2mE_k}$$

Where E_k is kinetic energy

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_k}}$$

If a charged particle carrying charge q is associated through a potential difference V volts, then kinetic energy $E_k = Qv$.

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mqV}}$$

The Heisenberg Uncertainty Principle:

It is impossible to know simultaneously both the momentum p (defined as mass time's velocity) and the position of a particle with certainty.

Stated mathematically we have:

$$\Delta x\, \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2\pi}$$

Postulates of Quantum Mechanics:

Postulate 1:

The properties of a quantum mechanical system are determined by a wavefunction Ψ(r,t) that depends upon the spatial coordinates of the system and time, r and t.

Postulate 2:

The wave function is interpreted as probability amplitude with the absolute square of the wave function, Ψ∗(r,t)Ψ(r,t) interpreted at the probability

density at time t. A probability density times a volume is a probability, so for one particle $\psi*(x_1,y_1,z_1,t)\psi(x_1,y_1,z_1,t)dx_1dy_1dz_1$ is the probability that the particle is in the volume dxdydz located at x_l,y_l,z_l at time t.

Postulate 3:

For every observable property of a system there is a quantum mechanical operator. The operator for position of a particle in three dimensions is just the set of coordinates x, y, and z, which is written as a vector

$r=(x,y,z)=xi^{\rightarrow}+yj^{\rightarrow}+zk^{\rightarrow}$

Postulate 4

The time-independent wave functions of a time-independent Hamiltonian are found by solving the time-independent Schrödinger equation.

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

Postulate 5:

The time evolution or time dependence of a state is found by solving the time-dependent Schrödinger equation.

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

Postulate 6:

If a system is described by the eigen function ψ of an operator A^ then the value measured for the observable property corresponding to A^ will always be the eigenvalue a, which can be calculated from the eigenvalue equation.

$$\hat{A}\psi = a\psi$$

Postulate 7:

If a system is described by a wave function ψ, which is not an eigen function of an operator A^, then a distribution of measured values will be obtained, and the average value of the observable property is given by the expectation value integral,

$$\langle A\rangle = \frac{\int \psi * A\ \psi d\tau}{\int \psi * \psi d\tau}$$

Operators:

an *operator* as "a rule that transforms a given function into another function''

$\int$ $+,-,\div,\times$ all are operator.

Linear Operator:

The operators occurring in quantum mechanics are linear.

$\hat{A}$ is a linear operator if and only if it has the following two properties:

$\hat{A}[f(x)+g(x)] = \hat{A}f(x) + \hat{A}f(x) + \hat{A}g(x)$ (i)

$\hat{A}[cf(x)] = c\hat{A}f(x)$ (ii)

Commutator Operator:

The commutator of two operators $\hat{A}$ and $\hat{B}$ denoted $[\hat{A}\hat{B}]$ is defined by:

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

and the anticommutator $\{\hat{A},\hat{B}\}$ is defined by:

$\{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$

Properties of Commutators:

Using the commutator relation, we can establish the following properties:

- Antisymmetry: $[\hat{A}\hat{B}] = -[\hat{B}\hat{A}]$
- Linearity: $[\hat{A},\hat{B}+\hat{C}+\hat{D}+\ldots] = [\hat{A},\hat{B}]+[\hat{A},\hat{C}]+[\hat{A},\hat{D}]+\ldots.$
- Hermitian conjugate of a commutator: $[\hat{A},\hat{B}]^{\dagger} = [\hat{B}^{\dagger},\hat{A}^{\dagger}]$
  $[\hat{A},\hat{B}\hat{C}] = [\hat{A},\hat{B}]\hat{C} + \hat{B}[\hat{A},\hat{C}]$
- Distributivity: $[\hat{A},\hat{B}\hat{C}] = [\hat{A},\widehat{B}],\hat{C} + [\hat{A},\hat{C}]\hat{B}$
- Jacobi identity: $[\hat{A},[\hat{B}\hat{C}]] + [\hat{B},[\hat{C},\hat{A}]] + [\hat{C},[\hat{A},\hat{B}]] = 0$

Hermitian Adjoint of Operators (†):

Every operator can be represented a square matrix. Therefore, Hermitian adjoint of an operator correspond to conjugate transpose of a matrix. It is denoted by

$$\hat{A}^{\dagger} = (A^{*})T = (AT)^{*}$$

General Property:

(1) $(A+B)^{\dagger} = A^{\dagger} + B^{\dagger}$

(2) $(A^{\dagger})^{\dagger} = A$

(3) $(AB)^{\dagger} = B^{\dagger}A^{\dagger}$

(4) $(A^{\dagger})^{n} = (A^{n})^{\dagger}$

(5) $ABCD\ |\Psi\rangle^{\dagger} = \langle\Psi|D^{\dagger}C^{\dagger}B^{\dagger}A^{\dagger}$

(6) $(aA)^{\dagger} = a^{*}A^{\dagger}$

Hermitian Operator

An operator $\hat{A}$ is said to be hermitian if $\hat{A}^{\dagger} = \hat{A}$

According to second postulate to every observable in classical mechanics, there corresponds an Hermitian operator in quantum mechanics.

An operator $\hat{A}$ is said to be hermitian if

$$\int \Psi^{*}\hat{A}\Psi d\tau = \int(\hat{A}\Psi)^{*}\Psi d\tau$$

Eigen value of' Hermitian opertor are real and eigen function of Hermitian operator are orthogonal.

Eigen function and Eigen value equation

Eigenvalue equation are those equation in which on the operating of a function by an operator, we get function back only multiplied by a constant value. The function is called eigen function and the corstant value is called eigen value.

Average Value of Kinetic Energy(E):

Normalised wave function for Simple Harmonic Oscillation

$$\Psi = \frac{\left(\frac{\beta}{\pi}\right)1}{4e^{\frac{-\beta x^2}{2}}}$$

$$\langle E\rangle = \int_{L.L}^{U.L} \Psi E \Psi^* d\tau$$

$$= \int_{-\infty}^{+\infty} (\frac{\beta}{\pi})^{\frac{1}{4}} e^{\frac{-\beta x^2}{2}} \frac{\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\left(\frac{\beta}{\pi}\right)1}{4e^{\frac{-\beta x^2}{2}}} dx$$

$$= \frac{\left(\frac{\beta}{\pi}\right)1}{4}\left(\frac{\beta}{\pi}\right)1 \frac{(-\hbar^2)}{2m}\int_{-\infty}^{+\infty} e^{\frac{-\beta x^2}{2}} \frac{\partial}{\partial x}\frac{\partial}{\partial x} e^{\frac{-\beta x^2}{2}} dx$$

$$= \frac{-\hbar^2}{2m} \frac{\left(\frac{\beta}{\pi}\right)1}{2\int_{-\infty}^{+\infty} e^{\frac{-\beta x^2}{2}} \frac{\partial}{\partial x}}\left(-\frac{\beta}{2}\right) 2x e^{\frac{-\beta x^2}{2}} dx$$

$$= \frac{-\hbar^2}{2m} \frac{\left(\frac{\beta}{\pi}\right)1}{2\int_{-\infty}^{+\infty} e^{\frac{-\beta x^2}{2}}}(-\beta)\left[-\frac{\beta}{2} 2x e^{\frac{-\beta x^2}{2}} x + e^{\frac{-\beta x^2}{2}}\right] dx$$

$$\frac{-\hbar^2}{2m}\frac{\left(\frac{\beta}{\pi}\right)1}{2}\beta 2\int_{-\infty}^{+\infty} e^{\frac{-\beta x^2}{2}} x 2 e^{\frac{-\beta x^2}{2}} dx + \frac{\hbar^2}{2m}\frac{\left(\frac{\beta}{\pi}\right)1}{2\beta}\int_{-\infty}^{+\infty} e^{\frac{-\beta x^2}{2}} e^{\frac{-\beta x^2}{2}} dx$$

$$= \frac{-\hbar^2}{2m}\frac{\beta^{\frac{5}{2}}}{\pi^{\frac{1}{2}}} 2\int_{-\infty}^{+\infty} x^2 e^{\frac{-\beta x^2}{2}} dx + \frac{\hbar^2}{2m}\frac{\beta^{\frac{3}{2}}}{\pi^{\frac{1}{2}}} 2\int_{-\infty}^{+\infty} x^0 e^{\frac{-\beta x^2}{2}} dx$$

$$= \frac{-\hbar^2}{2m}\frac{\beta^{\frac{5}{2}}}{\pi^{\frac{1}{2}}} 2 \frac{1}{2\beta^{\frac{3}{2}}}\Gamma\left(\frac{3}{2}\right) + \frac{\hbar^2}{2m}\frac{\beta^{\frac{3}{2}}}{\pi^{\frac{1}{2}}} 2 \frac{1}{2\beta^{\frac{1}{2}}}\Gamma\left(\frac{1}{2}\right)$$

$$= = \frac{-\hbar^2\beta}{2.2m} + \frac{\hbar^2\beta}{2m} = \frac{\hbar^2\beta}{4m}$$

$$= \frac{\hbar^2}{4m}\frac{\sqrt{k}\sqrt{m}}{\hbar}$$

$$= \frac{h}{2\pi 4}\sqrt{\frac{k}{m}} = \frac{h\vartheta}{4}$$

Average Value of Potential Energy (V):

$$V = \frac{1}{2} kx^2$$

$$\langle V\rangle = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} e^{\frac{-\beta x^2}{2}} \left(\frac{1}{2} kx^2\right) \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} e^{\frac{-\beta x^2}{2}} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \frac{1}{2} k \int_{-\infty}^{+\infty} x^2 e^{-\beta x^2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} \frac{k}{2} 2\int_{0}^{+\infty} x^2 e^{-\beta x^2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{\frac{1}{2}} k \frac{1}{2\beta^{\frac{3}{2}}}\Gamma(\frac{3}{2}) \left[\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2} = \frac{\pi^{\frac{1}{2}}}{2}\right]$$

$$= \frac{k}{4\beta} = \frac{k\hbar}{4\sqrt{mk}} = \frac{h}{4}\frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{h\nu}{4}$$

Orthonormal Condition:

If two wave function Ψ_m and Ψ_n (or, Ψ_i and Ψ_j) are such that $\int \Psi_m^* \Psi_n d\tau = 0$ or $\int \Psi_n^* \Psi_m d\tau = 0$

Then Ψ_m and Ψ_n are said to be orthogonal.

If m = n; in this condition, then

$\int \Psi_m^* \Psi_m d\tau = 1$ (normalised) and $\int \Psi_n^* \Psi_n d\tau = 1$ (normalised)

Linear Momentum and Angular Momentum

The classical definition of angular momentum $\vec{L} = \vec{r} \times \vec{p}$ depends on six numbers r_x, r_y, r_z, p_x, p_y and p_z . Translating this into quantum mechanical terms, the heisenberg uncertainty principle tells us that it is not possible for all six of these numbers to be measured simultaneously with arbitrary precision. Therefore, there are limits to what can be known or measured about a particles angular momentum. It turns out that the one can do is to simultaneously measure both the angular momentum vectors magnitude and its component along one axis.

Position Vector(x, y, z):

The component of position with commutative with self and other component is zero.

$$[x, y] = 0; \quad [y, z] = 0; \quad [y^2, x] = 0; \quad [x, x] = 0$$

Linear Momentum (p_x, p_y, p_z):

Component of linear momentum commuted with itself and with another component.

$$[p_x, p_y] = 0; [p_x, p_x^2] = 0; [x, p_x] \neq 0;$$
$$[x, p_y] = 0; [x, p_z] = 0; [x^2, p_z] = 0$$
$$[z, p_z] \neq 0; [p_x, x^2] \neq 0; [z, p_z] \neq 0;$$
$$[px, x^2] = i\hbar 2x; [x, p_x] = i\hbar$$
$$[z^2, p_y] = 0; [z^3, p_x] = 0; [z^4, p_z] = i\hbar^2 z^3;$$
$$[x^7, p_x] = i\hbar^7 x^6 [p_y, y^3] = -i\hbar^3 y^2 = \frac{\hbar}{i} 3y^2$$

Angular Momentum (L_x, L_y, L_z):

$$[L_x, L_y] = i\hbar L_z \quad [L_x, y] = i\hbar z \quad [L_x, x] = 0$$
$$[L_y, L_z] = i\hbar L_x \quad [L_y, z] = i\hbar x \quad [L_y, y] = 0$$
$$[L_z, L_x] = i\hbar L_y \quad [L_z, x] = i\hbar y \quad [L_z, z] = 0$$

Ladder Operator:

There are two types of Ladder Operators:

(1) $L_+ = L_x + iL_y$

(2) $L_- = L_x - iL_y$

Show that the commutation relation L_z with L_+.

(I) $[L_z, L_+] = [L_z, L_x + iL_y]$

$= [L_z, L_x] + i[L_z, L_y]$

$= i\hbar L_y + i[-i\hbar L_x]$

$= i\hbar L_y + i(-i\hbar L_x)$

$= i\hbar L_y + i(-i\hbar L_x)$

$= i\hbar L_y + \hbar L_x$

$= \hbar[iL_y + L_x]$

$= \hbar L_+$

Spin Matrices for Electron:

Like orbital angular momentum operators L_x, L_y, L_z, the spin operators S_x, S_y and S_z to be associated with the components of spin angular momentum satisfy the commutation relations.

$[S_x, S_y] = S_xS_y - S_yS_x = i\hbar S_z$

$[S_y, S_z] = S_yS_z - S_z S_y = i\hbar S_x$

$[S_z, S_x] = S_zS_x - S_xS_z = i\hbar S_y$

$\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3$

$S^2 = S_x^2 + S_y^2 + S_z^2 = \frac{\hbar^2}{4}(\sigma_x^2 + \sigma_y^2 + \sigma_z^2) = \frac{3}{4}\hbar^2$

The Time Independent Schrödinger Wave Equation:

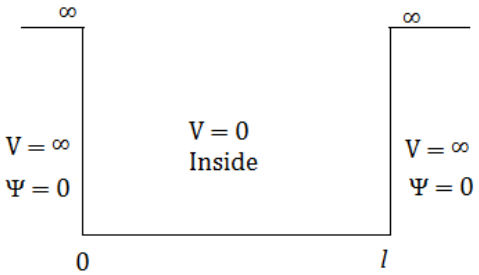
Schrödinger proposed that the wave function for a particle of mass m in one dimension is the solution to the equation

$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\Psi = E\,\Psi$

The Time Dependent Schrödinger Wave Equation

$H\Psi = i\hbar\frac{d\Psi}{dt}$ where i is the imaginary unit, defined to equal the square root of −1

The Particle in a One-Dimensional Box: A Simple Model



$\frac{d^2\Psi}{dx^2} = \infty\Psi$ or $\Psi = \frac{1}{\infty}\frac{d^2\Psi}{dx^2}$

That is $\Psi = 0$ outside the box. This means that the particle cannot exist outside the region O <x <l. Within the box, the schrodinger equation for the motion of the particle takes the form.

$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2}E\Psi = 0$

$\Rightarrow E = \frac{\alpha^2 h^2}{8\pi^2 m} = \frac{n^2 h^2}{8m\ell^2}$ .....(10)

Energy of a particle in 1-D box is quantized.

So energy difference between the two successive energy levels will be

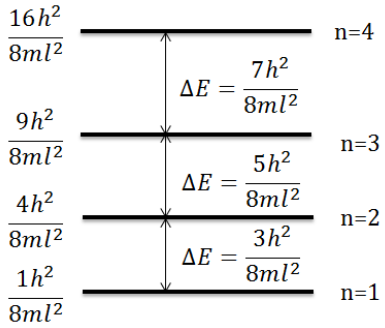
$\Delta E = E_{n+1} - E_n$

$\Delta E = \frac{(n+1)^2 h^2}{8m\ell^2} - \frac{n^2 h^2}{8m\ell^2} = \frac{[(n+1)^2 - n^2]h^2}{8m\ell^2} = \frac{(2n+1)h^2}{8m\ell^2}$

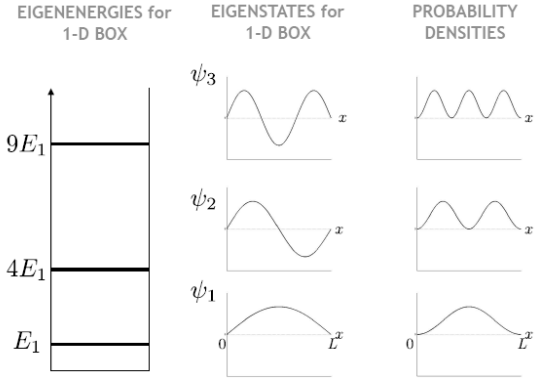
Zero-point energy (Ground state energy):

$E_{n=1} = \frac{h^2}{8m\ell^2}$

Energy Level Diagram in 1-D box:



Graph of Wave Functions and Probability:



Normalization of Ψ

Since the total probability of finding the particle within the box is 1, therefore, according to Born's interpretation of the wave function, the normalization of Ψ required that

$$\int_0^l \Psi_n^2\,dx = 1$$

$$\therefore \Psi = \sqrt{\frac{2}{l}}\,sin\left(\frac{n\pi x}{l}\right)$$

Particle in a symmetrical 1-D box from -l to +l:

Consider a free particle is confined to move in 1D box of length -l to +l.

V = 0 inside the box

V = ∞ else where

Schrodinger wave equation for 1-D box is

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

Or, $\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\,\Psi = 0$ (∵ V =0)

Or, $\frac{d^2\Psi}{dx^2} + k^2\Psi = 0$

$\because \Psi = ASinkx + BCoskx$ ...(1)

Possible Solutions:

(a) A = 0, cos k ℓ =0 ⇒ k ℓ =n$\frac{\pi}{2}$⇒k=$\frac{n\pi}{2\ell}$ (n=1, 3, 5....)

So, Ψ (x)=B cos ($\frac{n\pi x}{2\ell}$) (n=l,3,5...)

(b) B = 0, sin k ℓ =0 ⇒k ℓ = n$\frac{\pi}{2}$⇒ k= $\frac{n\pi}{2\ell}$ (n=2,4, 6....)

So, Ψ (x)=A sin ($\frac{n\pi x}{2\ell}$) (n = 2,4,6)

Boundary conditions:

(i) For first $\Psi = 0, x = -\ell$

0 = -A sin k ℓ + B cos k ℓ ....(2)

$\begin{bmatrix} sin(-\theta) = & -sin\theta \\ cos(-\theta) = & +cos\theta \end{bmatrix}$

(ii) $\Psi = 0, x = +\ell$

$0 = ASink\ell + BCosk\ell$ ....(3)

By addition of eqs. (2) and (3)

2Bcosk ℓ = 0

B cos k ℓ = 0 i.e. B = 0 or cos k ℓ = 0

By subtracting eq. (2) and (3)

-2Asink ℓ =0

A sin k ℓ =O i.e. A=0 or sin k ℓ =0

Particle in Two-Dimensional Box

Schrodinger wave equation for free particle for 2-D box:

$\frac{\partial^2\Psi(x,y)}{\partial x^2} + \frac{\partial^2\Psi(x,y)}{\partial y^2} + \frac{8\pi^2 m}{h^2} E\Psi(x, y) = 0$

$\Psi = \sqrt{\frac{2}{\ell}} \sin\frac{n_x\pi x}{\ell_x} \sqrt{\frac{2}{\ell}} \sin\frac{n_y\pi y}{\ell_y}$

$E = \frac{n_x^2 h^2}{8m\ell_x^2} + \frac{n_y^2 h^2}{8m\ell_y^2} = \frac{h^2}{8m}\left(\frac{n_x^2}{\ell_x^2} + \frac{n_y^2}{\ell_y^2}\right)$

If $\ell_x = \ell_y$ E=$\frac{h^2}{8ml^2}\left(n_x^2 + n_y^2\right)$

Degeneracy in 2-D box

Zero-point energy:

n_x=1 n_y=1 ⇒ $E_{11} = \frac{h^2}{4m\ell^2}$

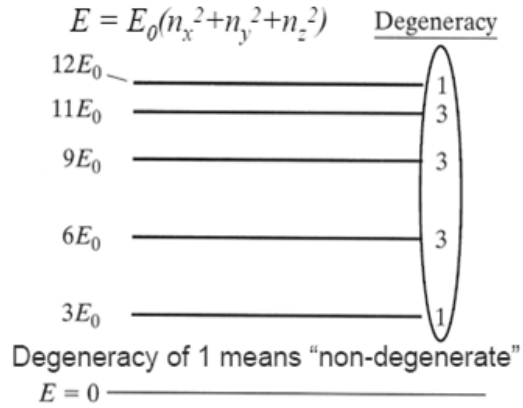
Particle in Three-Dimensional Box:

So three dimensional schrodinger equation.

$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi + \frac{8\pi^2 m}{h^2} E\,\Psi = 0$

Schrodinger wave equation for a particle in three dimension box.

$\frac{\partial^2\Psi(x,y,z)}{\partial x^2} + \frac{\partial^2\Psi(x,y,z)}{\partial y^2} + \frac{\partial^2\Psi(x,y,z)}{\partial z^2} + \frac{8\pi^2 m}{h^2}$



the normalized wave function of a three-dimensional box is

Ψ = XYZ = $\left(\sqrt{\frac{2}{\ell_1}} \sin\frac{n_x\pi}{\ell_1} x\right)\left(\sqrt{\frac{2}{\ell_2}} \sin\frac{n_y\pi}{\ell_2} y\right)\left(\sqrt{\frac{2}{\ell_3}} \sin\frac{n_z\pi}{\ell_3} z\right)$

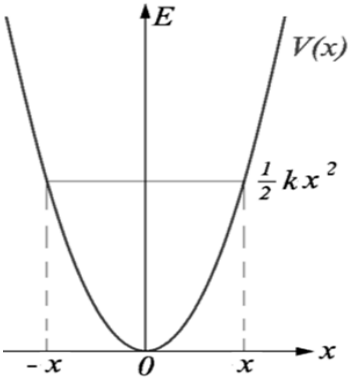
and total energy is

$E=E_x+E_y+E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{l_1^2} + \frac{n^2}{l_2^2} + \frac{n^2}{l_3^2}\right)$

Harmonic Oscillator

One-Dimensional Simple Harmonic Oscillator

If we plot potential energy of a particle executing simple harmonic oscillations as a function of displacement from the equilibrium position, we get a curve as shown in figure.



The vibrational frequency of the oscillator of mass m is given by:

$\upsilon = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2}$

The Hermite Polynomial of degree n is defined as:

$H_n(\xi) = (-1)^n e^{\xi^2}\left\{\frac{\partial^n\left(e^{-\xi^2}\right)}{\partial\xi^n}\right\}$

A few Hermite polynomials are given below:

$H_0(\xi) = 1$ $\quad H_3(\xi) = 8\xi^3 - 12\xi$

$H_1(\xi) = 2\xi$ $\quad H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$

$H_2(\xi) = 4\xi^2 - 2$

The normalized wave functions of the one-dimensional S.H.O. are then written as:

$\Psi_n(\xi) = \left(\frac{\beta^{1/2}}{2^n n!\sqrt{\pi}}\right)^{1/2} e^{-\xi^2/2} H_n(\xi)$

Where n= 0, 1, 2, 3,…

Energy of S.H.O. The energy of the S.H.O. is obtained by comparing Equations (11) and (12), where we find that:

α / β = 2n + 1

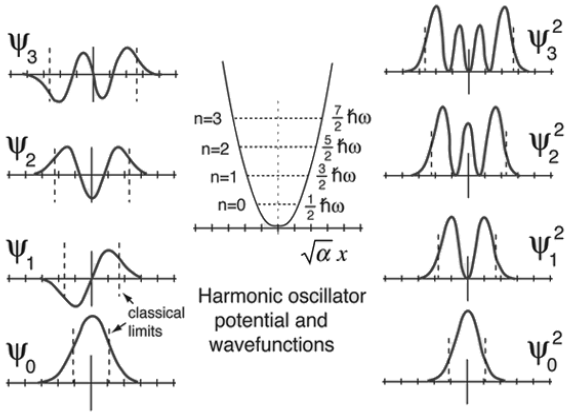
$$E = \left(n + \frac{1}{2}\right) \hbar \left(\frac{K}{m}\right)^{\frac{1}{2}}$$

The energy state with n = 0 is the vibrational ground state with energy

$$E_o = \frac{1}{2} h\nu$$

This energy is called the zero point energy of the oscillator.

Graph of wave function and probability:



Degeneracy for 2-D Harmonic Oscillator:

The energy, E = E_x + E_y

$E = \left(n_x + \frac{1}{2}\right)h\nu + \left(n_y + \frac{1}{2}\right)h\nu$

$E = h\nu\,(n_x + n_y + 1)$

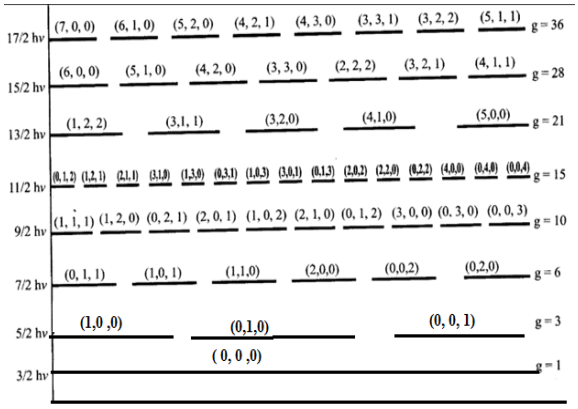
Degeneracy = $n_x + n_y + n_z$

n	n_x	n_y	degeneracy
0	0	0	1
1	10	01	2
2	201	021	3
3	3021	0321	4
4	40312	04132	5

Degeneracy for 3-D harmonic oscillator:

$E = \left(n_x + \frac{1}{2}\right)h\nu + \left(n_y + \frac{1}{2}\right)h\nu + \left(n_z + \frac{1}{2}\right)h\nu$

$E = \left(n_x + n_y + n_z + \frac{1}{2}\right)h\nu$



Virial Theorem:

According to the virial theorem, potential V α x^b

In SHO, V α x^2 → b = 2

⇒ 2 ⟨T⟩ =b ⟨V⟩ → 2 ⟨T⟩ = 2 ⟨V⟩

⇒ ⟨T⟩ = ⟨V⟩ …(1)

$\frac{\langle T\rangle}{\langle V\rangle}$ = 1:1

$\frac{\langle E\rangle}{\langle V\rangle} = \frac{\langle T\rangle + \langle V\rangle}{\langle V\rangle}$ …(2)

From equation (1) and (2),

$\frac{\langle V\rangle + \langle V\rangle}{\langle V\rangle} = \frac{2\langle V\rangle}{\langle V\rangle}$ = 2:1

$\frac{\langle E\rangle}{\langle V\rangle}$ = 2:1

Simple Harmonic Oscillator's formula

With the formula given below we can solve the problems of the Simple Harmonic Oscillator

(1) $\int_{-\infty}^{+\infty} x^n e^{-\propto x^2} dx = 0$ (if n = 1,3,5,……any odd number)

(2) $\int_{-\infty}^{+\infty} x^n e^{-\propto x^2} dx = \int_0^{+\infty} x^n e^{-\propto x^2} dx$ (n = even)

$= 2\frac{1}{2\alpha^{\frac{n+1}{2}}}\Gamma\left(\frac{n+1}{2}\right) \Rightarrow \int_0^{+\infty} x^n e^{-\propto x^2} dx = 2\frac{1}{2\alpha^{\frac{n+1}{2}}}\Gamma\left(\frac{n+1}{2}\right)$

Remark: $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$; $\Gamma\frac{3}{2} = \frac{1}{2}\sqrt{\pi}$

$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\frac{1}{2}\sqrt{\pi}$; $\Gamma\left(\frac{9}{2}\right) = \frac{7}{2}\frac{5}{2}\frac{3}{2}\frac{1}{2}\sqrt{\pi}$

Hydrogen Atom & Rigid Rotor

The basic for explaining the experimental spectra of hydrogen like species such as He^+, Li^{2+} and Be^{3+}. However, this theory was not entirely satisfactory as it failed to provide an interpretation of relative line intensities in the hydrogen spectrum and also and also failed completely when it was applied to explain the energies and spectra of more complex atoms in this section, we consider the application of Schrodinger's wave theory to one-electron atom, in the subsequent section, it will be shown how the principles of this theory can be applied, in a more approximate way, to many electron atoms.

Setting of Schrodinger Equation:

The time independent form of Schrodinger equation is

$H_{OP}\,\psi_{total} = E_{total}\,\psi_{total}$

$H_{OP} = T_{OP} + V_{OP} = (-\frac{h^2}{8\pi^2 m_e}\nabla_e^2 - \frac{h^2}{8\pi^2 m_e}\nabla_n^2) - \frac{Ze^2}{(4\pi\varepsilon_0)r}$

$[-\frac{h^2}{8\pi^2 m_e}(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial xz_e^2}) - \frac{h^2}{8\pi^2 m_n}\left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial xz_n^2}\right) - \frac{Ze^2}{(4\pi\varepsilon_0)r}]\,\psi_{total} = E_{total}\,\psi_{total}$

one involving the free movement of the centre of mass of the atom in space and the other involving the relative motion of the electron with respect to the nucleus within the atom.

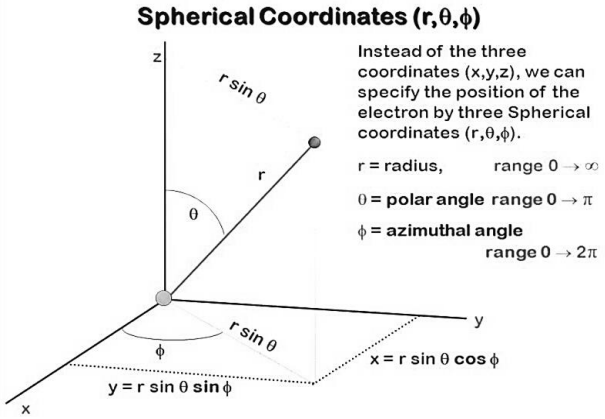
The two equations are:

$-\frac{h^2}{8\pi^2(m_e+m_n)}(\frac{\partial^2}{\partial x_c^2} + \frac{\partial^2}{\partial y_c^2} + \frac{\partial^2}{\partial xz_c^2})\,\psi_M = E_{trans}\,\psi_M$ ...(4)

$[-\frac{h^2}{8\pi^2\mu_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{(4\pi\varepsilon_0)r}]\,\psi_e = E\,\psi_e$ ...(5)

with $E_{trans} + E = E_{total}$

Schrodinger Equation in Terms of Spherical Polar Coordinates:



The solution of Schrodinger equation becomes very much simplified if the equation is expressed in the coordinate system that reflects the symmetry of the system. In the present case the potential energy field is spherical symmetry (V depends only on r), and thus, it is convenient to transform the Schrodinger equation (5) into the spherical polar coordinates r, θ and φ by using the relations

$X = r\sin\theta\cos\varphi$; $y = r\sin\theta\sin\varphi$; $z = r\cos\theta$

The transformation is lengthly and tedious process, and only the transformed expression is given below:

$[-\frac{h^2}{8\pi^2\mu r^2}\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\Theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\} - \frac{Ze^2}{(4\pi\varepsilon_0)r}]\Psi = E\,\Psi$

where ψ is a function of r, θ and φ

Radial Part of Hydrogen like Orbitals

n	l	Orbital Name	$R_{nl}(\bar{r})$; $\bar{r} = Zr/a_o$
1	0	1s	$2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\bar{r}}$
2	0	2s	$\frac{\sqrt{2}}{4}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(2-\bar{r})e^{-\bar{r}/2}$
	1	2p	$\frac{\sqrt{6}}{12}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\bar{r}e^{-\bar{r}/2}$
3	0	3s	$\frac{2\sqrt{3}}{243}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(27-18\bar{r}+2\bar{r}^2)\,e^{-\bar{r}/3}$
	1	3p	$\frac{2\sqrt{6}}{243}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}(6\bar{r}-\bar{r}^2)e^{-\bar{r}/3}$
	2	3d	$\frac{4\sqrt{30}}{2430}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\bar{r}^2 e^{-\bar{r}/3}$

Angular part of hydrogen like orbitals

l	m_l	Suborbital Name	$Y_{lm_l}(\boldsymbol{\Theta},\boldsymbol{\Phi})^*$
0	0	s	$\left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
1	0	p_z	$\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta$
	±1	px	$\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta\cos\Phi$
	±1	py	$\left(\frac{3}{4\pi}\right)^{\frac{1}{2}}\sin\theta\sin\Phi$
2	0	d_{z^2}	$\left(\frac{15}{16\pi}\right)^{\frac{1}{2}}[3\cos^2\theta - 1]$
	±1	d_{xz}	$\left(\frac{15}{16\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta\cos\Phi$
	±1	d_{yz}	$\left(\frac{15}{16\pi}\right)^{\frac{1}{2}}\sin\theta\cos\theta\sin\Phi$
	±2	d_{xy}	$\left(\frac{15}{16\pi}\right)^{\frac{1}{2}}\sin^2\theta\sin2\Phi$
	±2	$d_{x^2-y^2}$	$\left(\frac{15}{16\pi}\right)^{\frac{1}{2}}\sin^2\theta\cos2\Phi$

Virial theorem for hydrogen atom:

According to the virial theorem, $V \propto x^b$

In the Hydrogen atom, Potential:

$V \propto r^{-1} \rightarrow$

b = -1

2(T) = b (V)

2(T) = -(V)

$\frac{(T)}{(V)} = -\frac{1}{2} \rightarrow 2(T) = -(V)$

$\frac{(E)}{(V)} \pm \frac{-\frac{1}{2}(V)+(V)}{(V)} = \frac{1}{2} \rightarrow \frac{(E)}{(V)} = \frac{1}{2}$

Where, E = total energy

T = kinetic energy

V =potential energy

V = -2T (Virial Theorem for Hydrogen atom)

Degeneracy in H-atom:

(1) If a spin is not included degeneracy = $\boldsymbol{n^2}$ (where, n is principle quantum number)

(2) If spin is included degeneracy = $\boldsymbol{2n^2}$

The Rigid Rotor

A diatomic molecule rotating about an axis perpendicular to the inter nuclear axis and passing through the centre of gravity of the molecule constitutes an example of a rigid rotor, it being assumed that the inter nuclear distance does not change during rotation. The kinetic energy (K.E.) of the molecule is given by

$$K.E. = T = \frac{1}{2} I\omega^2 = \frac{L^2}{2I}$$

The angular momentum L = Iω. If no force acts on the rotor, we can set the potential energy V = 0. Hence, the Hamiltonian is expressed as

$$H = T + V = \frac{L^2}{2I}$$

The expression for L^2 in spherical polar coordinates (r,θ, $\emptyset$) is given by

$$L^2 = h^2 \left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\emptyset^2}\right]$$

The Schrödinger equation $\hat{H}\Psi = \hat{E}\Psi$ may thus be written as

$$\frac{1}{2I}\left[-h^2\left\{\frac{1}{sin\theta}\frac{1}{\partial\theta}\left(sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2\Psi}{\partial\emptyset^2}\right\}\right] = E\Psi$$

THE SCHRODINGER EQUATION AND DE BROGLIE WAVES

The particle in a box model provides an illustration of the fact that the energy Eigen function represents de Broglie waves. In the case of zero potential energy

$$E = \frac{1}{2}mv^2 = \frac{P^2}{2m}$$

Where we use the definition of the momentum, **p = mv**. From the de Broglie wavelength formulae

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

This is same as:

$$E = \frac{h^2}{2m\lambda^2}$$

The energy of a de Broglie wave is inversely proportional to the square of its wavelength. The wavelength of the wave function is the value of x such that the argument of the sine function equal to 2π

$$\frac{n\pi\lambda}{a} = 2\pi$$

$$\lambda = \frac{2a}{n}$$

As the value of n increases, the energy increases, the wavelength decreases and the number of nodes increases. It is an important general fact that a wave function with more nodes corresponds to a higher energy.

TUNNELLING

Stationary states in a Barrier Potential:

The potential barrier, which is defined as:

V = 0	for x < 0	Region I
$V = V_0$	for 0 < x < L	Region II= 0
V= 0	for x > L	Region III

The Reflectance (R):

$$R = \frac{\text{magnitudeofreflectedcurrent}}{\text{magnitudeofincidentcurrent}}$$

$$R = \frac{(p_1-p_2)^2}{(p_1+p_2)^2}$$

The transmittance (T):

$$T = \frac{\text{magnitudeoftransmittedcurrent}}{\text{magnitudeofincidentcurrent}} = \frac{4(p_1p_2)}{(p_1+p_2)^2}$$

Let the 2 electron of H_2 designed by (1) and (2) and the 2 nuclei a and b.

The wave function of the molecule:

$$\Psi_{AB} = C_1\Psi_1 + C_2\Psi_2$$

Where, $\Psi_1 = \emptyset_a(1)\,\emptyset_b(2)$

$\Psi_2 = \emptyset_a(2)\,\emptyset_b(1)$

Bonding M.O. = $\Psi_+ = N_+ [\emptyset_a(1)\,\emptyset_b(2) + \emptyset_b(1)\,\emptyset_a(2)]$

Antibonding M.O. = $\Psi_- = N_- [\emptyset_a(1) + \emptyset_b(2) - \emptyset_b(1)\,\emptyset_a(2)]$

$N_- = \frac{1}{2(1-s^2)}$

, normalised wave functions:

$\Psi_+ = \frac{1}{\sqrt{2(1+s^2)}}[\emptyset_a(1)\emptyset_b(2) + \emptyset_a(2)\emptyset_b(1)]$

$\Psi_- = \frac{1}{\sqrt{2(1-s^2)}}[\emptyset_a(1)\emptyset_b(2) - \emptyset_b(1)\emptyset_a(2)]$

For symmetric function

$$\Psi_1 = \phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)$$

For antisymmetric function,

$$\Psi_2 = \phi_1(1)\,\phi2(2) - \phi_1(2)\,\phi2(1)$$

$$\Psi_3 = \phi_1(1)\phi_2(2)$$

$$\Psi_4 = \phi_1(2)\phi_2(1)$$

The normalization factor for linear combination is $\frac{1}{\sqrt{2}}$ but there are two additional concern (1) Spin and (2) Pauli

(1) Spin function must be included special function to describe the state.

(2) Pauli principle are also required that complete wave function must be antisymmetric to exchange the electron.

$$\Psi(1,1) - \Psi(2,2) \rightarrow Antisymmaetric$$
$$\Psi(1,2) - \Psi(2,1) \rightarrow Symmetric$$

Spin Part:

α (1) α (2)→symmetric

$$\beta\ (1)\ \beta\ (2) \rightarrow symmetric$$
$$\frac{1}{\sqrt{2}}\ [\alpha(1)\ \beta\ (2)\ +\ \beta(1)\ \alpha(2)] \rightarrow \text{symmetric}$$
$$\frac{1}{\sqrt{2}}\ [\alpha(1)\ \beta\ (2) -\ \beta(1)\ \alpha(2)] \rightarrow \text{antisymmetric}$$

Spatial Part:

$$\phi_a\ (1)\phi_b\ (2)\ \rightarrow \text{symmetric}$$
$$\phi_a\ (2)\phi_b\ (1)\ \rightarrow \text{symmetric}$$
$$\frac{1}{\sqrt{2}}\ [\phi_a\ (1)\phi_b(2) +\ \phi_a(2)\phi_b(1)] \rightarrow \text{symmetric}$$
$$\frac{1}{\sqrt{2}}\ [\phi_a(1)\phi_b(2)\ -\ \phi_a(2)\phi_b(1)] \rightarrow \text{antisymmetric}$$

The pauli exclusion principle may be stated as follow: The wave function of electron must be antisymmetric with respect to any interchange of electron, Partial with half integral (spin) are required antisymmetric wave function and refer to as fermions.

Partial with half integral spin are required symmetric wave function refer as Bosons.

$$\Psi\ =\ \Psi_{spatial}\ \Psi_{spin} \rightarrow \text{(antisymmetry)}$$
$$\Psi\ \rightarrow\ \Psi_{symmetry(spatial)}\ \Psi_{antisymmetry(spin)} \rightarrow \text{(antisymmetric)}$$
$$\Psi\ \rightarrow\ \Psi_{antisymmetry(spatial)}\ \Psi_{symmetry(spin)} \rightarrow \text{(antisymmetric)}$$

Determinant form of the wave functions (Slater Determinants)

For an n-electron atom, there are n rows and n columns.

$$\Psi_ = \frac{1}{\sqrt{n!}} \begin{vmatrix} A(1)B(1) & \dots \\ A(2)B(2) & \dots \\ \dots & \dots & \dots \\ \dots & \dots & \dots \\ A(n)B(n) & \dots \end{vmatrix}$$

VARIATION PRINCIPLE

There are a number of such methods

- Perturbation method
- Variation method

According to variation principle it can be shown that, if Ψ_0 is the correct wave function for a system, whose correct energy is E_0then any other acceptable wave function Ψ_1 will give energy greater than E_0.Energy for any trial wave function can be calculated using conventional formula.

$E_i = \frac{\int \Psi^* H \Psi d\tau}{\int \Psi^* \Psi d\tau}$ (Because we don't know that the trial wave function is normalized or not)

$E_i \geq 0$

Application:

% error in energy by using variation principle and cross check of the function's validity.

% error = $\frac{E_i - E_0}{E_0} \times 100\%$

If % error is negative, function is not acceptable.

PERTURBATION

First Order Perturbation:

Perturbation theory is an approximation method to find out the exact solution of any system with great accuracy. We disturb the operator in a specific order.

Equating the coefficient of zero order on λ

$$H_0\ |\phi_n^0\rangle = \ \varepsilon_n^0 |\phi_n^0\rangle$$

- **First order on λ**

$$H_0|\Psi_n^{(0)}\rangle\ +\ \omega|\Psi_n^{(0)}\rangle = \ \varepsilon_n^0\ |\Psi_n^{(1)}\rangle + \ \varepsilon_n^{(1)}|\Psi_n^{(0)}\rangle$$

ω the corrected term.

Second order on λ

$$H0|\Psi_n^{(2)}\rangle\ +\ \omega|\Psi_n^{(1)}\rangle = \ \varepsilon_n^0\ |\Psi_n^{(2)}\rangle + \ \varepsilon_n^{(1)}|\Psi_n^{(1)}\rangle + \ \varepsilon_n^{(1)}|\Psi_n^{(1)}\rangle + \ \varepsilon_n^{(2)}|\phi_n^0\rangle$$

$$\varepsilon_n^{(2)} = \left[\frac{\langle\phi_m^0\ |\omega|\phi_n^0\rangle|\ \phi_m^0\rangle}{\langle\varepsilon_n^0 - \varepsilon_m^0\ \rangle}\right]$$

$$\varepsilon_n^{(2)} = \ \sum\langle\phi_m^0\ |\omega|\phi_m^0\rangle|\ \left[\frac{\langle\phi_m^0\ |\omega|\phi_m^0\rangle}{\langle\varepsilon_n^0 - \varepsilon_m^0\ \rangle}\right]$$

Second Order Perturbation

It is the correction to the energy i.e. based on the function that is modified during 1st order perturbation energy. For the second order perturbation the energy state never be equal.

The energy correction for second order is this:

$$E_n^2 = \sum_{m \neq n} \frac{\langle\phi_m^0\ |W|\phi_n^0\rangle^2}{\langle E_n^0 - E_m^0\ \rangle}$$

If n = m then value becomes zero.

MOLECULAR ORBITAL THEORY

Hydrogenic Energy Levels

For a hydrogenic atom of atomic number, Z they are given by

$E_n = -\frac{hcR_H Z^2}{n^2}$

The value of l species the magnitude of the orbital angular momentum through $[\ell(\ell+1)]^{1/2}\hbar$ with ℓ = 0, 1, 2 we can think of ℓ as indicating the rate at which the electron circulates around the nucleus.

Electron Spin

The magnitude of the spin angular momentum is given by the expression {s (s + 1)} h, so for an electron this magnitude is fixed at $\frac{1}{2}\sqrt{3\hbar}$ for any electron.

Nodes:

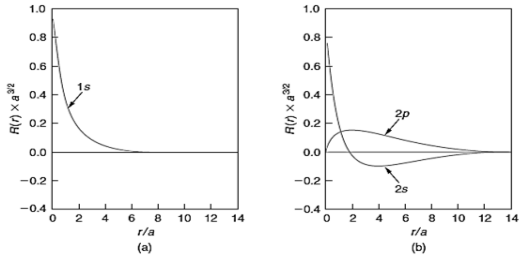
Regions where wave function pass through zero are called nodes.

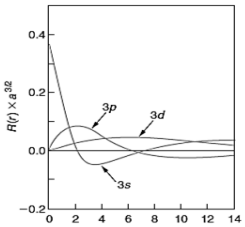
Consequently, there are two types of nodes. Radial nodes occur where the radial component of the wave function passes through zero and angular nodes occur where the angular component of the wave function passes through zero. The numbers of both types of node increase with increasing energy and are related to the quantum numbers n and l.

The Radial Variation of Atomic Orbitals:

An s orbital has nonzero amplitude at the nucleus; all other orbitals (those with l>0) vanish at the nucleus.

Figure below; show the radial variation of some atomic orbitals. A 1s orbitals, the wavefunction with n = 1, l = 0 and m_s =0, decays exponentially with distance from the nucleus and never passes through zero.





The Radial Distribution Function:

A radial distribution function gives the probability that an electron will be found at a given distance from the nucleus, regardless of the direction.

The total probability of finding the electron in a spherical shell of radius r and thickness dr is the integral of $\psi^2 d\tau$ over all angles. This result is written P(r) dr, where P(r) is called the radial distribution function. In general.

$P(r) = r^2 R(r^2)$

In general, this most probable distance decrease as the nuclear charge increases (because the electron is attracted more strongly to the nucleus), and specifically.

$r_{maximum} = \frac{a_0}{Z}$

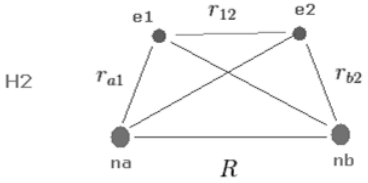
The lowest-Energy Wave function:

The formula for the normalized, wave function

$$\Psi(r) = \left(\frac{1}{\sqrt{\pi}}\right)\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} exp\,(-Zr/a_0)$$

SYMMETRIC AND ANTISYMMETRIC WAVE – FUNCTIONS OF HYDROGEN MOLECULES:

When two H atoms meet a molecule is not always formed. The two atoms repel each other if the spins of two electrons are parallel (↑↑) and two atoms attract each other if the spin of two electrons are antiparallel (↓↑). The system consists of two hydrogen nuclei 'a' and 'b' and two electrons whose coordinates are denoted by symbols 1, 2; r_{12} the distance between two electrons 1 and 2.



$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{1}{4\pi\varepsilon_0 r_{a1}} - \frac{1}{4\pi\varepsilon_0 r_{a2}} - \frac{1}{4\pi\varepsilon_0 r_{b1}} - \frac{1}{4\pi\varepsilon_0 r_{b2}} + \frac{1}{4\pi\varepsilon_0 r_{12}} + \frac{1}{4\pi\varepsilon_0 R}$$

we have for two electrons four spin functions:

	Electron 1	Electron 2
α (1) α(2)	↑	↑
β (1) β(2)	↓	↓
α (1) β(2)	↑	↓
α (1) β(1)	↓	↑

Orbital	Spin	Total S
$\psi_a(1)\psi_b(2)$ + $\psi_a(2)\psi_b(1)$	$\alpha(1)\beta(2)$- $\alpha(2)\beta(1)$	0
		1

Each α describes the spin $+\frac{1}{2}$ and β describes the spin $-\frac{1}{2}$

Since two electrons are indistinguishable from each other, so we choose linear combination of the four functions, ∝ (1) ∝ (2) and $\beta(1)\ \beta(2)$ are already symmetrical. Instead of ∝ (1) β (2) and $\beta(2)$ ∝ (1) we choose ∝ (1) β (2) + ∝ (2) β (1) symmetrical function and ∝ (1) β (2) - ∝ (2) β (1) antisymmetrical function.

$$\left.\begin{matrix} & m_2 \\ \alpha(1)\alpha(2) & +1 \\ \alpha(1)(2)+\alpha(2)\beta(1) & 0 \\ \beta(1)\beta(2) & -1 \\ \alpha(1)\beta(2)-\alpha(2)\beta(1) & 0 \end{matrix}\right\}$$ with S=1 with S=0

Approximation of Linear Combination of Atomic Orbitals: the form of the MO should be such that it has characteristic possessed separately by Ψ_A and Ψ_B, i.e. the MO should be reduciable to AOs in the extreme cases.

The only choice is to take MO as the linear combination of atomic orbitals.

Mathematically, it written as:

$$\Psi_{mo} = C_1\Psi_A + C_2\Psi_B$$

Physical Significance of Coefficients in a LCAO MO:

Since the electron distribution is given by the square of the wave function, the electron distribution for the function given by equation (1) is

$$\Psi_{Mo}^2 = C_1^2\Psi_A^2 + C_2^2\Psi_B^2 + 2C_1C_2\Psi_A\Psi_B$$

The normalization criterion applied to Ψ_{mo} gives

$$\int \Psi_{Mo}^2\, d\tau = 1 = C_1^2\int \Psi_A^2 d\tau + C_2^2\int \Psi_B^2 d\tau + 2C_1C_2\int \Psi_A\Psi_B d\tau$$

atomic orbitals to be normalized, we get

$C_1^2 + C_2^2 + 2C_1C_2S_{AB}$=1

Where S_{AB} is the overlap integral between the orbitals Ψ_A and Ψ_B. In the zero-overlap approximation (S_{AB} =0) the normalization condition is

$C_1^2 + C_2^2$ = 1

HUCKEL MOLECULAR ORBITAL THEORY

1. Basic Assumptions

1. The atomic orbitals contributing to the π-bonding in a planar molecule (e.g. the so-called pπ orbitals in a molecule such as benzene) are antisymmetric with respect to reflection in the molecular plane; they are therefore of a different symmetry to the atomic orbitals contributing to the σ-bonding and may be treated independently.
2. H_{ii} is assumed to be the same for all the carbon atom involved. It is usually represented by the symbol α (unknown) and is called the coulomb integral.
3. H_{ij} is assumed to have the constant value β if atom i and j are bounded directly, it is called exchange integral.

   Exchange integral = $H_{ij} = \int \phi i\, H\phi_j d\tau = \beta$ when i=j are directly bonded = 0 if atoms i and j are non-bonded
4. All overlap integrals representing the overlap of atomic orbitals centred on different atoms are neglect.

   $S_{ij} = \int \phi_i\, \phi_j d\tau = 0$ when i≠ j= 1 when i= j .

   Since the atomic orbitals are normalised

F or the non-trivial roots we set n x n **secular determinant** equal to zero.

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \dots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \dots & H_{2n}-ES_{2n} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & \dots & H_{3n}-ES_{3n} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & \dots & H_{4n}-ES_{4n} \\ \dots & \dots & \dots & \dots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \dots & H_{nn}-ES_{nn} \end{vmatrix} = 0$$

$$\begin{bmatrix} \alpha-E & \beta & 0 & 0 & 0 & \dots \\ \beta & \alpha-E & 0 & 0 & 0 & \dots \\ 0 & 0 & \alpha-E & \beta & 0 & \dots \\ 0 & \beta & 0 & \alpha-E & 0 & \dots \\ \beta & 0 & 0 & 0 & \alpha-E & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{bmatrix}$$

Ethylene Molecule: $H_2C{=}CH_2$

$$\begin{bmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{bmatrix} = 0$$

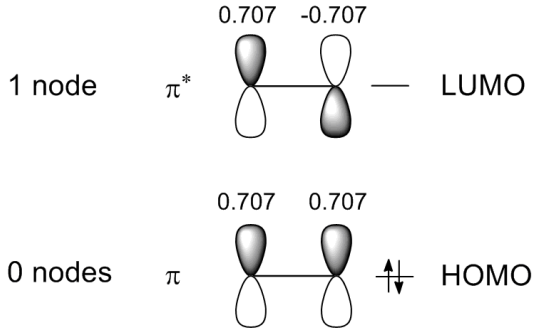
The sum of the squares of the coefficients is always unity.

Molecular orbital	x	E	C_1	C_2	Number of nodes
Bonding	-1	$\alpha+\beta$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0
Antibonding	1	$\alpha-\beta$	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	1

The two normalized wave functions corresponding to two Hückel molecular orbitals for ethylene as:

$$\Psi_{BMO} = \frac{1}{\sqrt{2}}\Psi_1 + \frac{1}{\sqrt{2}}\Psi_2$$

$$\Psi_{BMO} = \frac{1}{\sqrt{2}}\Psi_1 + \frac{1}{\sqrt{2}}\Psi_2$$



Butadiene Molecule

$\Psi_1 = 0.372\ \Psi_{2pz(1)} + 0.602\Psi_{2pz(2)} + 0.602\ \Psi_{2pz(3)} + 0.372\ \Psi_{2pz(4)}$

$\Psi_2 = 0.602\ \Psi_{2pz(1)} + 0.372\Psi_{2pz(2)} - 0.372\ \Psi_{2pz(3)} - 0.602\ \Psi_{2pz(4)}$

$\Psi_3 = 0.602\ \Psi_{2pz(1)} - 0.372\Psi_{2pz(2)} - 0.372\ \Psi_{2pz(3)} + 0.602\ \Psi_{2pz(4)}$

$\Psi_4 = 0.372\ \Psi_{2pz(1)} - 0.602\Psi_{2pz(2)} - 0.602\ \Psi_{2pz(3)} + 0.372\ \Psi_{2pz(4)}$

Cyclobutadiene

Energy = $2(\alpha + 2\beta) + 2\alpha$

$\therefore$ Delocalization energy = $2(\alpha + 2\beta + 2\alpha) - 4(\alpha + \beta) = 0$