1.1 INTRODUCTION

Five-membered aromatic heterocyclic fragments are part of various organic compounds having vast applications in the field of biology, pharmacology, material sciences and agriculture. Their importance can be recognized from the fact that majority of the published work in organic chemistry involves at least heterocyclic ring [1-3]. The heterocyclic molecules are well known for their significant role as mediators in synthetic reactions for preparing functionalized materials. Heterocyclic intermediates are utilized in synthesis as protecting groups, readily produced and also eliminated [4-5]. Heterocyclic systems are present in biology as various cofactors, nucleic acid bases and amino acid residues [6-7]. There are numerous drugs containing heterocyclic ring structures. The application of metallated heterocyclic reagents in the synthesis of numerous molecules of biological, pharmacological and material science interest signifies the value of their anionic species as well [8-10]. There are numerous industrial sectors like electronics, photonics, sensors and corrosion protection which have realized the importance of organic heterocycles [11]. Among the simplest heterocycles are the five-membered aromatic rings containing one or two heteroatoms. These compounds can undergo reactions such as oxidative ring openings, Diels-Alder construction, cycloaddition and photocycloadditions [12].

Furan, thiophene and its derivatives are vital organic materials which are extensively used in organic synthesis [13-14]. Furan and its derivatives are released into the atmosphere by various sources (e.g. the combustion of fossils fuels, plants and biomass burning etc.) and act as primary pollutant [15]. The primary biological characteristics of furan have found significant applications as fungicides, herbicides, disinfectants and therapeutic agents. Moreover it has also drawn attention due to its capability in preventing the growth of mold and bacteria in aqueous suspensions of starch, glue etc [16]. Further to this, various other derivatives of furan such as methylfuran and tetrahydrofuran are used in the process of polymerization as monomers and also as solvents [17]. Thiophene polymers and oligomers have attracted lot of research and have been studied extensively due to their extraordinary electronic and
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optical properties [18]. Especially in the field of consumer electronics, polythiophene has been used in manufacturing electronic devices in form of conductors [19], electrode materials [20] and organic semiconductors [21]. Polythiophene and its derivatives have a large and very rapid nonlinear optical response [22]. Due to natural existence of thiophene in some plant products, its diversified applications in synthetic pharmaceuticals and dyestuffs are also well justified [23].

Heterocyclic azoles are recognized as the building blocks of numerous antibiotic, anticancer agents, fungicides and other drugs [24-25]. Pyrrole occurs largely in nature and is a structural part of porphyrin of heme, chlorophyll and vitamin B12 [26]. The five-membered heteroring such as furan, thiophene and pyrazole are used for development of technical classes of dyes [27]. The one or more nitrogen containing heterocyclic ring is vital constituent part of biological compounds such as purines (adenine (I), guanine (II)), pyrimidine (thymines, cytosines), sympathomimetic amines (histamine (III), serotonin (IV)), amino acids (tryptophan, histidine) [4,28].

Pyrazole is involved in the N-H···N hydrogen bond network in their crystals with a number of hydrogen bonding patterns: dimer, trimer, tetramer, hexamer, and catemer [29-30]. Pyrazole derivatives have numerous applications as herbicides in pharmaceutical
industry and in medicinal chemistry. Their inherent characteristics have made possible their use for the purpose of various biological activities such as antitumour [31], antimicrobial [32], anti-inflammatory [33], antiviral [34], anticonvulsant [35] and antidepressant [36].

One of the essential amino acids, histidine (V), contains a heterocyclic imidazole ring in its chemical structure. Histidine is present in several proteins and enzymes and plays a vital part in the structure and binding functions of hemoglobin. One of the applications of imidazole is in the purification of histidine-tagged proteins in immobilized metal affinity chromatography. Imidazole is used to elute tagged proteins bound to Ni ions attached to the surface of beads in the chromatography column. An excess of imidazole is passed through the column, which displaces the histidine-tagged from nickel co-ordination, freeing the histidine-tagged proteins. One of the most common applications of imidazole is through tea leaves and coffee beans due to its association with theophylline molecule and this is known to stimulate central nervous system [37]. Moreover, histamine which is a decarboxylation product of histidine plays an important function in living system as a contracting agent of smooth muscles and as a constituent in allergic reactions. The other important amino acid tryptophan (VI) and many naturally occurring alkaloids are indole derived structures [28].

There are so many compounds which contain imidazole ring and exhibit different type of pharmacological and biological activities. Some compounds like clonidine (VII), guanfacine and lofexidine hydrochloride act as $\alpha_2$-adrenergic agonist and clinically used for treatment of attention deficit hyperactivity disorder by affecting part of brain that controls attention and impulsivity. These drugs may also used for controlling blood pressure and neuropathic pain. The metronidazole and nitrosoimidazole act as
bactericidal, imidazole-2-one as antileishmanial [38]. The α2-adrenergic antagonists like idazoxan (VIII) and napamezole are undergoing clinical evaluation as antidepressant [39]. The agents like 1-vinylimidazole [40], 5-nitroimidazole [41], megazole etc. find their applications as antiprotozoal, antimicrobial, anticonvulsant, muscle relaxant, antiulcer, gastric motility stimulators. Mercaptopurine includes imidazole in its chemical structure is anticancer medication used to fight against leukemia [38].

![Structure VII](image1.png)

![Structure VIII](image2.png)

Imidazole has been used widely as a corrosion inhibitors for copper and it alloys, iron and for zinc in acid chloride solutions [42-44]. Many compounds of industrial and technological importance contain imidazole derivatives. The thermostable polybenzimidazole contains imidazole fused to a benzene ring and linked to benzene, and acts as a fire retardant. Imidazole is also found in a variety of compounds which are used for photography and electronics. Heterocyclic nitrogen restraining functional groups e.g. pyrrole, pyrazole, imidazole etc. are renowned in organic fuels such as coal and biomass [45]. Imidazole and many of its derivatives outline a class of nucleophilic and general base catalysts [46-47]. Atmospheric and combustion chemistry attracts application of high temperature reactions of five- and six-membered nitrogen containing heterocycles due to function of these compounds in the production of the pollutants NO and NO₂ (NOₓ) during combustion process [48-49].

Isoxazole and its derivatives are vital structural units that have been found to be part of various molecules of biological interest. Isoxazole containing molecules, such as sulfamethoxazole and oxacilin, have been in general medical use for many years [50]. Isothiazole derivatives find applications as various pharmacological activities such as anti-inflammatory [51], antiviral [52] analgesic and antibacterial [53]. The drug containing pyrazole-isothiazole derivative was synthesized for cure against Cryptococcus
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Neoformans which is the root of the most frequent life-threatening fungal infection in patients with AIDS [54]. Selenazoles have been broadly studied as synthetic tools [55] as well as for their biological significance [56]. There is huge class of peptide natural products that comprise one or more of the five-membered ring heterocycles such as oxazoles and thiazoles. These structures have drawn attention because of their interactions with diverse intracellular targets and mechanism of heterocycle biosynthesis. As noted in, Gly-Ser dipeptides moieties would yield the aminomethyloxazole moiety and Gly-Cys dipeptides moieties would yield the corresponding thiazole heterocycle [57]. Fused oxazole have been found to exhibit insecticidal, sedative, tranquilizer, antiepileptic and antitubercular activities [58].

Nature incorporates this oxazole into several architecturally attractive specimens as in antibiotics berninamycin A (IX) [59], griseovirdin and virginiamycin M (X) [60]. Over the years, biological activities are associated with thiazole derivatives [61]. Development of various drugs found applications of thiazole for the purpose of treatment of allergies [62], hypertension [63], inflammation [64], schizophrenia [65], bacterial [66], HIV infections [67], hypnotics [68] and very recently as fibrinogen receptor antagonist with antithrombotic activity for treating pain [69] and also as new barriers of bacterial DNA Gyrase B [70]. Several molecules of biological interest such as thifluzamide (XI) (antifungal drug) with trade name abasol cream, epothilones (XII) (anticancer),

\[ \text{IX} \]

\[ \text{X} \]
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sulfathiazol (antimicrobial drug), ritonavir (antiretroviral drug), and bleomycine and tiazofurin (antineoplastic drug) have thiazole moiety [71].

![Image of molecule XI]

![Image of molecule XII]

Commercial significant thiazoles include mainly dyes. The anthroquinone dyes contain benzothiazole subunits: algol yellow 8, indanthren rubin B etc. These thiazoles dyes are used for dying cotton. It is shown that the suitable replacement of benzene-ring structures by thiazole rings in polar donor-acceptor molecules enhances in the nonlinear optical susceptibilities [72]. The thiazole derivatives containing benzothiazoles is also found in firefly chemical luciferin (XIII) [73].

![Image of molecule XIII]

Saturated heterocyclic systems with chalcogens have varied medicinal and biochemistry applications, playing important role as anticonvulsants, antiarrhythmic, bactericides, fungicides and anticancers. Tetrahydrofuran is frequently used in polymer science [74]. Tetrahydrofuran dissolves poly vinyl chloride as well and is the main ingredient in poly vinyl chloride adhesive. It can be utilized to liquefy old poly vinyl chloride cement [75]. Tetrahydrofuran finds applications in hydroboration reaction to synthesize primary alcohols and as a solvent for organometallic compounds such as organolithium and Grignard reagents [76]. Tetrahydrofuran is vital structure unit in a variety of biologically important molecules [77]. Derivatives of tetrahydrofuran are broadly prescribed for a various diseases such as nucleosides antibiotic, for e.g.
azidothymidine (XIV) is acknowledged as the first anti-AIDS drug used in antiviral chemotherapy and prophylaxis in the United States [78]. Tetrahydrothiophene is used as ligand in chemistry [79]. Tetrahydropyrrole is found in the leaves of tobacco, beer, coffee and carrot. The tetrahydropyrrole ring structure is present in numerous natural alkaloids such as nicotine and hygrine. It is found in many pharmaceutical drugs such as procyclidine and bepridil. It also form basis for racetum compounds and central structure of the amino acids such as proline and hydroxyproline [80]. Tetrahydropyrrole is used as a building block in the synthesis of many complex compounds. In organic chemistry, tetrahydropyrrole is used to activate ketones and aldehydes toward nucleophilic addition by formation of enamines [81].

Pyrazolidine moiety is common among non-steroidal anti-inflammatory drugs such as ampyrone, phenzone, feprazone etc [82-83]. Oxazolidines and thiazolidines thiones are important heterocyclic compounds that have been studied along with a variety of their derivatives [84-86]. The oxazolidine derivative, oxazolidinediones are used as anticonvulsants [87]. Natural and modified valonia extracts and oxazolidines are employed as tanning materials [88]. Oxazolidines as cross linking agent play an important role in the physical properties of collagen based biomaterials [89-91]. The drug which contains a thiazolidine ring is the antibiotic drug pencillin (XV) where R is the variable group [92]. The drug pioglitazone (XVI) contains thiazolidine ring. It is drug usually indicated in case of type II diabetes for decreasing blood sugar. It also decreases triglycerides and C-reactive protein levels. Selenium containing compounds provide protection against cancer [93]. Series of selenzolidines have been evaluated in the salmonella typhimurium TA98 tester strain and are found to posses antimutagenic
activity [94]. Imidazolidines and their derivatives comprise a class that has shown anticonvulsive, anti-schistosome, antiamebic, antibacterial, anti-inflammatory and antiarrhythmic pharmacological activities [95]. Hydantoine derivatives are an important class of compounds with anti-shistosomiasis and anticonvulsant activities i.e. imidazolidine-2,4-dione [96-97].

The five-membered heterocyclic nitrogen containing systems such as pyrazole, imidazole, thiazolidine, pyrazolidine have found immense applications and have been subjected to tremendous research for the development of various drugs in the field of antibacterial, fungicidal, anti-inflammatory, anticonvulsant, diuretics and antihistamine etc. Thus these wide horizons of applications of heterocyclic molecules drive the importance of researching and understanding the hydrogen bonding ability, acidity and basicity as well as their ability to lose hydride of selected five-membered heterocyclic molecules. (In order to distinguish between aromatic and saturated heterocyclic molecules, they are labeled with ‘r’ and ‘s’ alphabet along with the number designating the molecules respectively.)

**HYDROGEN BONDING INVOLVING HETEROCYCLIC MOLECULES**

The hydrogen bonding interactions are important because these interactions play influential role in determining the shapes, properties and functions of number of biomolecules [98]. Water being the most abundant and vital for life, the contact with the biomolecules is unavoidable. The water is known as active participant in biochemical processes [99-101]. Thus the intermolecular hydrogen bond between the water and molecules of biological interest is crucial in rationalizing of the mechanism governing the biochemical processes. There is remarkable use of hydrogen bonding in supramolecular assemblies, material chemistry, crystal packing, mineralogy, organic chemistry and organometallic structures [102-103]. Enhancement of the rate of reaction has been
achieved due to the existence of hydrogen bonds at the active site of enzymatic reactions. The enzyme holds the substrate at active site through a variety of interactions such as hydrogen bonding, dipole-dipole interaction, van der Waals interaction etc [104-105]. Many models predict the solubility and transport behavior of drug molecules on the basis of number of hydrogen bond sites exists [106-108]. The structure of α helix and β sheets of polynucleotide are shaped by hydrogen bonding [109-110]. The hydrogen bonds play an essential role in holding soft organic and inorganic matter such as DNA and liquid water [111].

**PROTONATION/DEPROTONATION AFFINITIES OF HETEROCYCLIC MOLECULES**

Protonation/deprotonation constitutes a pivotal role in chemistry [112] and biological [113] mechanisms. Their importance in protein folding and acid catalyzed enzymatic reactions is well recognized. The catalytic activity of many enzymes relies on upon proton transfer from one residue to another or to the substrate in one step or another [114]. The three dimensional structure of peptides and their biological activities are readily influenced by protonation [115]. A number of important addition/elimination reactions are recognized to be acid catalyzed [116]. The exchange of protons in heterocyclic molecules serves as an important aspect of electrophilic substitution mechanism with proton as electrophile [117]. The proton affinity helps in understanding fragmentation pattern in mass spectroscopy [118]. Elucidation of polyfunctional molecules have been resulted with the help from preferred site of protonation [119]. The estimations of protonation/deprotonations have been found to contribute towards empirical studies in two corresponding ways [120]

1. To foretell new molecular systems incorporating desired characteristics.
2. To evaluate the information using straightforward and relevant chemical concepts.

**HYDRIDE AND ELECTRON TRANSFER**

Hydride transfer has been recognized as significant reaction in chemistry of hydrocarbon and hydrocarbon derivatives and is known to occur in various forms. Most prominently it occurs in gas phase [121-122], in liquid super acids [123-124], on surface of solid-acid catalyst [125] and in biological system [126]. It also finds in applications in
reduction of ketones [127], aldehydes [128], alkenes [129], alkyl halide [130], imines [131] and hydrogen oxidation [132]. All these are examples of reactions which are proposed to occur via hydride transfer reactions. Ideally organic hydride donors serve as a model of natural organic hydride donors in chemical and biochemical reactions. Naturally produced organic hydride donors such as NAD(P)H [133], FADH$_2$ [134], ascorbic acid [135], tetrahydrofolate [136] play very important roles in the processes of biological reduction and bio-antioxidants. In many biological hydride transfer reactions, organic cofactors such as NADH/NAD$^+$ (Nicotinamide adenine dinucleotide), NADPH/NADP$^+$ and FADH/FAD$^+$ are involved. These reactions are engaged in the heterolytic cleavage and formation of C-H bonds [137-138]. Among the man made organic hydride donors, five-membered heterocyclic compounds have attracted the attention of chemist and biochemist [139]. The present study inquires into the possible pathways for hydride transfer as well as the hydride transfer ability of heterocyclic molecules.

Electron transfer attracts significant attention in chemistry for playing an important role in biological reactions such as enzyme functions, photosynthesis and proteins containing metal ion which can adopt different oxidation states via electron transfer [140]. Single electron transfer reactions in solution belong to a major research area in inorganic chemistry [141]. Electrospray [142] and thermospray [143] ionization techniques are also used to produce multiple charged gas phase biological species. Photoelectron spectroscopy has seen dramatic expansion during last few decades and has found to stand out as an extremely reliable technique for investigation of electronic structure of atoms and molecules. This has also contributed for empirical analysis of bonding characteristics of orbitals and their mutual interactions [144]. The electron transport properties in molecular wires made of heterocyclic molecules (pyrrole, furan and thiophene) by using Green’s function technique have been investigated [145]. Electron transfer reactions have been much studied both in gas phase and in solution [146]. Electron transfer is often immediately facilitated by several further reactions. Estimation of definite importance of heteroatoms in chemical and biochemical systems has been contributed research associated with electron transfer in heterocyclic molecules. Electron transfer in heterocyclic molecules helps in estimating the specific role of heteroatoms in chemical and biochemical systems.
1.2 REVIEW OF LITERATURE
1.2.1 HYDROGEN BONDING OF HETEROCYCLES WITH OTHER MOLECULES

Several groups of scientists have shown their interest in hydrogen bonding interactions involving heterocyclic molecules. Jiang et al. have studied intermolecular hydrogen bond interaction of furan-HCl and furan-CHCl$_3$ complexes at the 6-31G** and 6-311+G** basis sets using ab initio calculations. Analyzing the hydrogen bond C(Cl)-H···O and C(Cl)-H···π interactions, it has been shown that for the complexes furan-CHCl$_3$, C-H bond length contracts while for the furan-HCl, H-Cl bond length elongates. The charge transfer from the lone pair of the proton acceptor into σ* antibonding orbital has been suggested on the basis of NBO analysis. In the furan-HCl complex, the H-Cl stretching frequency was observed to be red shifted while in case of furan-CHCl$_3$, C-H stretching frequency was blue shifted [147].

Further computational study of intermolecular complexes of furan with hydrogen halides (HX where X = F, Cl, Br, I) have been examined by Dong-Mei Huang et al. using ab initio calculations at the 6-311++G(d,p) basis set. Two types of geometries were observed, atom-on type geometry in which hydrogen bond acceptor and donor were coplanar and face-on geometry where the hydrogen bond donor was orientated perpendicular to the plane of the acceptor ring. The furan-HF and furan-HI complexes acquired atom-on and face-on type orientations, respectively. Both geometry types were obtained for the HCl- and HBr-furan complexes. The HF and HBr subunits of the atom-on complexes deviated to small extent from the furan ring plane whereas in furan-HCl complex, HCl molecule donated linear hydrogen bond to O atom lone pairs as shown in XVII. The interaction between the hydrogen of halides and the C2-C4 π-bond of the furan ring was observed in face-on type geometries. Interaction energy decomposition reported that electrostatic interactions made the primary contribution to the atom-on type complexes while orbital and electrostatic interactions dominated in the face-on type complexes [148].
Samanta et al. carried out study on interactions between pyridine with water, ammonia and methane using HF and MP2/6-31G(d,p) calculations. Interaction of water with pyridine is shown in XVIII. The pyridine accepted hydrogen bonds at the N atom along with that number of other orientations were also optimized in which X-H (X=N, O, and C) were placed above the π-face of the pyridine ring. The highest stabilization was obtained where water and ammonia were directly above the pyridine N whereas for methane, its carbon atom was shifted halfway between nitrogen and the ring centre. The corresponding complexation energies were 2.9 (X = O), 1.8 (N) and 1.0 (C) kcal/mol. The dispersion forces contributed in interaction with C-H bonds. The strength of π-facial hydrogen bonding was nearly the same for benzene and pyridine but the latter has shown a greater variation over the ring surface [6].

The study of hydrogen bonding properties of O and N in aromatic heterocycles using crystal data base structure and theoretical calculations was carried out by Nobeli et al. The study have been performed on the complexes of methanol with pyridine, pyrimidine, pyrazine, pyridazine, oxazole, isoxazole, 1,2,4-oxadiazole and furan as model for the heterocyclic fragments. The single point ab initio calculations of the interaction energy were carried out using intermolecular perturbation theory at the 6-31G** basis set. Intermolecular perturbation theory was used to obtain electrostatic forces, exchange-repulsion, polarization, dispersion and charge transfer terms. Surveys of the cambridge structural database for hydrogen bond between C(sp3)-O-H and aromatic fragments showed that nitrogen has better hydrogen acceptor ability as compared to oxygen. Minima on intermolecular potential surface obtained using model potential was observed to be typically deeper for the nitrogen than for oxygen acceptors although the hydrogen bond strength and geometry was influenced by other heteroatom in the ring and agreed well with the observed orientation in the data base. [149].

The hydrogen bonding involving four isotopmers [32S]-thiophene···H35Cl, [32S]-thiophene···H37Cl, [32S]-thiophene···D35Cl, [34S]-thiophene···H35Cl have been studied through rotational spectrum obtained using Fourier transform microwave spectrometer by
S.A. Cooke et al. The rotational constants, centrifugal distortion constants and Cl-nuclear quadrupole coupling constants were determined. The investigation of the spectroscopic constants led to the conclusion that the observed complex has $C_5$ symmetry, in which thiophene-HCl molecules were not coplanar but perpendicular and the hydrogen bond was of the $\pi$ type. This suggested that the S atom of thiophene is weaker hydrogen bond acceptor than the $\pi$ electron system. The geometry was such that the Cl atom was placed above the centroid of the thiophene ring, and the Cl-H vector points at the side of the S atom [150].

Nagy et al. carried out theoretical study on the hydration of pyrrole, imidazole and protonated imidazole in the gas phase and aqueous solution. The total geometry optimization of gas phase monomers and dimers were carried out using HF/6-31G* and MP/6-31G* levels and free energy calculations for the gas phase have been evaluated at MP2/6-311++G**/MP2/6-31G* theoretical level. The structure of the dilute aqueous solution of pyrrole, imidazole and protonated imidazole obtained utilizing optimized potentials for liquid simulations (OPLS). The in-plane adduct formation of pyrrole was preferred by 1.8 kcal/mol over the out of plane hydrated form (XIX). The in-plane hydration of imidazole ring was favored by 1.7 kcal/mol at the N1 site as compared to the N3. The statistical perturbation method in Monte Carlo simulations was used to predict relative solvation energy terms. The relative solvation free energy of imidazole referred to pyrrole was -4.1 kcal/mol, and the relative solvation enthalpy was -10 to -12 kcal/mol. The hydrogen bond geometric parameters in solution obtained using the OPLS were compared to the values in the gas-phase monohydrates at MP2 level. The only difference between OPLS and MP2 results were found for the neutral imidazole hydration at N3 site. In dilute aqueous solution the pyrrole molecule formed a hydrogen bond of N-H···O type in the molecular plane. The neutral imidazole forms two hydrogen bonds, one in ring plane N1-H···O hydrogen bond. Other form in which water molecules was hydrated the N3 site and were located in the $\pi$-region formed weaker bonds to the solute. The protonated imidazole formed two
strong in-plane hydrogen bonds of N-H···O type in aqueous solution with several water molecules in the π-region [151].

The hydrogen bonded complexes between C₄H₄Y (Y= O, S) and BX₃ (X = H, F, Cl) have been optimized at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) theoretical levels by Wang et al. Six conformers were obtained for the complexes. The AIM theory and NBO have been performed. The charge transfers were obtained using NBO analysis to study covalent character in complex. All the conformers were formed with p-π type interactions between C₄H₄Y and BX₃, in which the aromatic rings offer their lone pair electron to the empty p orbital of boron atom. From NBO analysis, it was observed that the furan homologues have formed stable conformers with the BX₃ molecules as compared to the thiophene-BX₃ systems. The stabilization energies fall within the range of -7.26 to -32.57 kJ/mol and -8.45 to -21.01 kJ/mol in furan-BX₃ and thiophene-BX₃ systems respectively [152].

The hydrogen bond interaction between water and imidazole (XX) was investigated with the matrix-isolation Fourier transform infrared spectroscopy by Van Bael et al. Three RHF, B3LYP and MP2 computational methods and for all three of them the 6-31++G** and 6-31G** basis sets were employed. The optimized geometry of imidazole by all three methods was in good agreement with the structure obtained experimentally. The matrix spectra of the two isomeric hydrogen bond complex species N-H···OH₂ and N···H-OH was performed and compared with the theoretically predicted IR frequencies and intensities. The experimental spectra of N-H···OH₂ have shown relative strong perturbations of the NH stretching and in-plane and out-of-plane deformation modes and weak perturbations of the bonded proton acceptor. On the other hand, the N···H-O-H complex of imidazole, which was about equal in strength compared to the isomeric N-H···OH₂ complex, induces stronger perturbations of the bonded water modes [153].

Bandyopadhyay et al. analyzed σ, π and χ types interactions of phenol with different molecules HF, HCl, H₂O, H₂S, NH₃, PH₃, MeOH, MeSH using MP2/6-31+G*
and MP2/aug-cc-pVDZ theoretical methods. Symmetry-adapted perturbation theory calculations on the MP2/6-31+G* geometries were obtained to analyze the components of interaction energies. The structures, binding energies, hydrogen bond length, charge transfer, vibrational spectra, IR intensity, thermochemical properties and dipole moment were explored and compared with experimental results. The correlations between electrostatic energy with the hydrogen bond length, charge, charge transfer and dipole moment were analyzed and inferred that HF favored $\sigma_O$-type hydrogen bonding, while $H_2O$, $NH_3$, and $MeOH$ favored $\sigma_H$-type hydrogen bonding. The $HCl$, $H_2S$, and $PH_3$ favor $\pi$-type hydrogen bonding, which are slightly favored over $\sigma_O$, $\sigma_H^*$, $\sigma_H^-$ type bonding, respectively. $MeSH$ favored $\chi_H$-type bonding, which has characteristics of both $\sigma_O$- and $\sigma_H^-$ hydrogen bonding [98].

Biswal et al. studied the hydrogen bonding interaction of p-cresol with tetrahydrofuran and tetrahydrothiophene. The existence of a single conformer of the p-cresol tetrahydrofuran and two conformers of the p-cresol tetrahydrothiophene complex was observed by Fluorescence Detected IR (FDIR) spectra. The change in the OH frequency in these complexes was recorded using FDIR spectroscopy. With the help of computed IR spectra and AIM analysis, the two conformers of p-cresol tetrahydrothiophene assigned were p-cresol with tetrahydrothiophene ($C_2$)/tetrahydrothiophene ($C_5$). All the AIM criteria for hydrogen bond have shown that O-H$\cdots$S hydrogen bond relatively weaker than O-H$\cdots$O hydrogen bond. The NBO analysis indicated the smaller extent of overlap between sulfur (LP) and $\sigma^*_H-O$ as compared to oxygen (LP) and $\sigma^*_H-O$ which in turn supported greater red shift of OH frequency for the p-cresol tetrahydrofuran complex as compared to those for the conformers of the p-cresol tetrahydrothiophene. The binding energy of the p-cresol tetrahydrofuran calculated to be 7.42 kcal/mol was about $\sim$20% greater than that of p-cresol tetrahydrothiophene. These binding energies were of the same order as those for the acyclic analogs, diethyl ether and diethyl sulfide. The diethyl ether and tetrahydrofuran consist of same number of carbon atoms but the dispersion energy contribution was much higher (43%) for diethyl ether than that for tetrahydrofuran (30%). In the case of sulfur analogs, it was similar ($\sim$50%) in the case of both diethyl sulfide well as tetrahydrothiophene complexes [154].
Ab initio and DFT calculations have been performed for the hydrogen bonded complexes of tetrahydrofuran with H2O, HF and NH3 by P.K. Sahu et al. with 6-311+G** and aug-cc-pVDZ basis sets. Their results indicated larger distortion in the geometry of tetrahydrofuran upon hydrogen bonding to NH3 where the C2 symmetry of tetrahydrofuran changed but relatively small variation in geometry was seen in hydrogen bonded tetrahydrofuran-H2O and tetrahydrothiophene-HF. The hydrogen bonding strength was found to be in the order HF > H2O > NH3 which was characterized by the order in the bond angles O2H15F14, O2H16O14, and O2H15N14 closer to the linearity and in terms of red shift associated with hydrogen bond donors [155].

Rotational spectrum of tetrahydrothiophene with water complex (C4H832S···H2O) have been studied by M.E. Sanz et al. by free jet millimeter wave absorption and molecular beam Fourier transform microwave spectroscopy. The rotational parameters have been studied in terms of geometry in which water molecule acted as proton donor lying close to the plane bisector to the angle CSC of tetrahydrothiophene. The interaction was inferred between the proton donor (water) and the nonbonding electron pairs of the S atom for tetrahydrothiophene. The free hydrogen was entgegen (E) to the ring. The O-H···S hydrogen bond was nearly linear with distance 2.37 Å, the deviation from collinearity of the atoms S···H-O is suggested from 162.12°. The entgegen (E) conformer corresponded to the global minimum [156].

M.E. Sanz et al. group also reported the ground-state rotational spectra of five isotopic species, C4H832S···H35Cl, C4H832S···D37Cl, The 4H832S···D35Cl, C4H832S···D37Cl and C4H834S···H35Cl in the frequency range 6-18.5 GHz using a molecular beam Fourier transform microwave spectrometer. With the help of spectral analysis, rotational, quartic centrifugal distortion and Cl- nuclear quadrupole coupling constants were determined for each isotoptomer. The rotational and quadrupole coupling constants have been interpreted in terms of geometry in which hydrogen chloride lies on the plane bisector to the \( \angle \text{CSC} \) of tetrahydrothiophene. The angle between the S···Cl internuclear line and the line bisecting the \( \angle \text{CSC} \) was found to be 86.6(7)° and the distance of r(S···Cl) =3.48(3) Å. The deviation of atoms S···H-Cl involved in the hydrogen bond from a collinear arrangement was estimated to approximate 14° [157].
1.2.2 PROTON TRANSFER

The proton affinities of series of azoles have been determined by Meot-Ner et al. using pulsed high-pressure mass spectrometry. They reported values in kcal/mol, isoxazole, 202.3; oxazole, 207.8; 1,2,4-triazole, 212.4; pyrazole, 212.8; thiazole, 213.2; imidazole, 222.1; 4-methylimidazole, 224.8; 1-methylimidazole, 228.0. They also carried out the theoretical calculations of the proton affinities at MP2/6-31G(d,p) level and obtained approximate same values as experimental results. They predicted preferred protonation site on the basis of theoretical and experimental data and suggested protonation of imidazole and oxazole at N3 was favored over N1 and O protonation by 53 and 57 kcal/mol respectively. The protonation occurred at N4 rather than N2 in 1,2,4-Triazole. The computed difference between N4 and N2 protonation of 1,2,4-Triazole was 13.3 kcal/mol. The correlation between lone pair n orbital energies and proton affinities was also studied [158].

The proton affinities of unsaturated and saturated heterocyclic molecules such as furan, 2-methylfuran, 3-methylfuran, thiophene, pyrrole, isoxazole, isothiazole, pyrazole, 3-methylpyrazole, 4-methylpyrazole, 5-methylpyrazole, oxazole, thiazole, imidazole, 2-methylimidazole, 4-methylimidazole, 5-methylimidazole, tetrahydrofuran, oxetane, oxepane, methyl ethyl ether, methyl propyl ether, diethyl ether, tetrahydrofuran, 1,4-dioxane, methyl butyl ether and many more have been calculated by Kabli et al. using G3 composite ab initio method. The calculations verified that heteroaromatic molecules with a single N, O or S atom protonate preferentially on a C α atom. Five-membered heteroaromatic molecules with more than one heteroatom and a pyridine-type N tend to get protonated principally on pyridine-type N. The presence of methyl group in the ring of the five-membered heteroaromatic molecules enhanced the proton affinity of the species without altering the thermochemically preferred site of protonation. From proton affinity difference between methyl ethyl ether, methyl propyl ether, diethyl ether it was revealed that additional methyl group at the α carbon atom increases the proton affinity by approximate 20 kJ/mol, whereas additional methylene group further removed from the oxygen atom increases proton affinity by 5-6 kJ/mol. Their theoretical computed results were in agreement with the experimental values and the proton affinities of
tetrahydrofuran and tetrahydropyran were observed to be same. The decrease in proton affinity was observed when additional oxygen atoms were introduced in the ring into the saturated heterocyclic bases [159].

Experimental study on the protonation of heterocyclic molecules like furan and pyrrole in gas have been done by Lorenz et al. Protonated furan (C₄H₅O⁺) and pyrrole (C₄H₆N⁺) have been produced by chemical ionization of respective parent molecule in the cell of Fourier transform ion cyclotron resonance mass spectrometer using CH₅⁺/C₂H₅⁺ as protonating agent. The protonation site was investigated in the 900–1700 cm⁻¹ fingerprint range by resonant infrared multiphoton dissociation (IRMPD) spectroscopy utilizing the free electron laser at the Centre Laser Infrarouge Orsay. The proton affinity at B3LYP/6-311G(2df,2pd) level have also been computed for comparison which revealed that Cα protonated isomers were only observed corresponding to the global minima on the potential energy surface of both protonated heterocyclic molecules. The less stable isomers corresponding to protonation at the Cβ atom or at the heteroatom were not detected by spectroscopic features but both Cα protonated isomers were identified. The IRMPD spectrum of the furan radical cation has been detected as well. Comparison of the IR spectra of the neutral molecules with the IRMPD spectra of the radical cation and the protonated species revealed that both ionization and protonation effected structural properties of these heterocyclic molecules [160].

Beelen et al. determined experimentally the evaluation of proton affinities of furan, 2-, 3-, and 4-methylphenols and the related anisoles with Fourier transform ion cyclotron resonance mass spectrometry and theoretically with the ab initio G3(MP2) calculations. The proton affinity of furan computed to be 812 kJ/mol determined on the basis of the experimental equilibrium constant for the proton transfer to acetone. This value was higher than that suggested in the literature (803 kJ/mol). The proton affinity of 2-position in furan was calculated to be 814 kJ/mol with G3(MP2) method observed to be in good agreement with experimental value. The experimental values of proton affinities revealed that 3-isomer was more basic than the 2-isomer, which in turn was more basic than the 4-isomer for both series of methylphenols and methylanisoles. The results of the
theoretically computed proton affinity of the most basic site within a methylphenol were in good agreement with the experimental values. The calculations revealed that the 4-position was the most basic site of the 2- and 3-methyl-substituted-phenols, whereas the 2- and 4-position in 4-methylphenols were almost equally basic. The replacement of the phenolic hydrogen with a methyl group in the methylphenols lead to an increase in the proton affinity approximate 20 kJ/mol, irrespective of the positions of the methyl group on the aromatic rings [161].

Rao et al. studied the proton affinity of 24 five-membered heterocyclic amines evaluated at HF/6-311++G**, B3LYP/6-31G*, B3LYP/6-311++G**, MP2/6-311++G** and G3B3 levels. The considered molecules include pyrrole and series of substituted pyrazoles, imidazoles, triazoles and thiazoles. The proton affinities of most azoles considered were much higher as compared with pyrrole since azoles were electron rich as compared to pyrrole and protonation disrupted aromaticity in pyrrole whereas in azoles aromaticity retained even after protonation. It has been observed that with increase in methyl substitution at pyrazole and imidazole proton affinities increases. The higher substitution by the alkyl group makes the electron rich, thereby increasing the proton affinity of the substituted compounds. The proton affinity values at B3LYP/6-311++G** and G3B3 levels were in good agreement with experimental values [162].

The acidities of azoles like pyrrole, pyrazole, imidazole, 1,2,3 triazole, 1,2,4 triazole, 1,2,5 triazole, 1,3,4 triazole, 1,2,3,4 tetrazole, 1,2,3,5 tetrazole and 1,2,3,4,5 pentazole in gas phase and in DMSO using ab initio and DFT methods determined by Vianello et al. They concluded that acidity increases with the number of nitrogen atoms in the ring achieving its maximum in pentazoles [163].

1.2.3 HYDRIDE AND ELECTRON TRANSFER

The reactivities of five-membered heterocycles in hydride transfer reactions have been explored by Lee et al. The rate of oxidation of 2-heteroaryl-1,3-dimethylbenzimidazoline derivatives 3H and 4H compounds have been carried out by 1-benzyl-3-carbamoylpyridinium ion, 1 and 1-benzyl-5-nitroisoquinolinium ion, 2 as shown in Scheme 1.2.3.1. The reactivities of the five-membered heterocycles failed to
The $pK_a$ appeared to depend mainly on the inductive effect of the heteroatoms and the variations in $k_2$ (rate constant) emerged to depend more on resonance involving the heteroatoms. When plot was drawn for rate constants for oxidation by the 1-benzyl-5-nitroisoquinolinium ion against rate constants for oxidation by 1-benzyl-3-carbamoylpyridinium ion of same imidazoline derivatives, a linear plot was obtained. These results widen the generality of the one-step mechanism of hydride transfer, without the involvement of high-energy intermediates [164].

M. Poyatos investigated imidazolidines as hydride source for the formation of transition-metal monohydrides. The reaction of a series of imidazolidines with chloro complex of Ir, Rh and Ru leads to the formation of corresponding monohydrido metal species. Theoretical analysis of the reduction process recommended that the reaction
proceeds via imidazolidine coordination followed by β-hydride elimination and resulted into metal hydride and the imidazolinium cation as the only reaction products. When large excess of the imidazolidine was added no over reduction has been observed. [165].

Computational studies directed at elucidating the mechanism of the oxidation of benzyl alcohol by liver alcohol dehydrogenase have been carried out by P.K. Agarwal et al. This enzyme reaction brings about hydride transfer from the alcohol substrate to the nicotinamide adenine dinucleotide coenzyme and a proton relay that deprotonates the alcohol substrate. Schematic illustration of the active site of LADH with a benzyl alcohol substrate and NAD$^+$ cofactor is shown Scheme 1.2.3.2. The dark arrows indicate the hydride transfer reaction and the first three steps of the proton relay (denoted PT1, PT2, and PT3). The alcohol deprotonation occurs prior to the hydride transfer step and that the alcohol deprotonation facilitates the hydride transfer by lowering the barrier for hydride transfer have been supported by electronic structure calculations at various levels of theory and classical molecular dynamics simulations. In this mechanism, the alcohol deprotonation led to formation of zinc-bound alkoxide ion, and the following hydride transfer resulted in benzaldehyde product [166].

Kil et al. carried out study on primary kinetic isotope effects (KIEs), $k_H/k_D$, spectrophotometrically for the reactions of NAD$^+$ analogues (acridinium ions $1a^+\cdot e^+$ and quinolinium ion, $2^+$) with heteroaromatic compounds such as 3-methyl-2 phenylbenzothiazoline, $3H(D)$, and 1,3-dimethyl-2-phenylbenzimidazoline, $4H(D)$ as shown in Scheme 1.2.3.3.
The KIEs decrease from 6.24 to 3.93 as the equilibrium constant \((K)\) was increased from about 1 to \(10^{12}\) by the structural variation in the hydride acceptor. The Marcus theory of atom transfer in a linear, triatomic model of the reaction, with tunneling, elucidated the variation of KIE with \(K\). The Marcus theory is based on a model involving no high energy intermediates, leading to a one-step mechanism. This study by group satisfied this condition [167].

Several 1-benzyl-1,4-dihydronicotinamide (BNAH) derivatives, which are important NADH (XXI) model compounds were studied theoretically in acetonitrile by Wang et al. All the calculations were performed with Gaussian 03. The performances of various DFT methods including B3LYP, B1B95, B3PW91, MPW1B95, MPWKCIS, and M06 were tested to determine the redox potentials. A substituted 1-benzyl-1,4-dihydronicotinamide was converted to oxidized form by the redox reactions. The multistep redox processes of BNAH consisted of three steps as shown in Scheme 1.2.3.4. The important thermodynamic properties of BNAHs were explored and the suggested mechanism for hydride transfer progress was pursued. The systematic study was carried out to investigate the para-substituent effect on the discrepancies of redox potentials and ionization potential [168].
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Scheme 1.2.3.4: Possible paths of hydride transfer

The ionization energies (IEs) and heats of formation (ΔH°(f)/ΔH°(298)) for thiophene (C₄H₄S), furan (C₄H₄O), pyrrole (C₄H₄NH), 1,3-cyclopentadiene (C₄H₆CH₂) and borole (C₄H₄BH) were calculated by Po-Kam Lo et al. using ab initio CCSD(T)/CBS approach. The respective CCSD-(T)/CBS predictions for C₄H₄S, C₄H₄O, C₄H₄NH, and C₄H₆CH₂, being 8.888, 8.897, 8.222, and 8.582 eV, were in excellent agreement with the experimental values of IE attained from photoelectron and photoion measurements. The CCSD(T)/CBS computed ΔH°(f)/ΔH°(298) predictions for C₄H₄S/C₄H₄S⁺, C₄H₄O/C₄H₄O⁺, C₄H₄NH/C₄H₄NH⁺ and C₄H₆CH₂/C₄H₆CH₂⁺ were also in good agreement with the available experimental data. The similar CCSD(T)/CBS IE and ΔH°(f)/ΔH°(298) predictions for C₄H₄BH thermodynamic data were not readily accessible due to its reactive nature. The CCSD(T)/CBS calculated IE(C₄H₄BH) value was 8.868 eV, and ΔH°(f)/ΔH°(298) values for C₄H₄BH and C₄H₄BH⁺ were 269.5 and 1125.1 kJ/mol respectively [169].

The electron-transport properties of various amino or nitro group substituted thiol-ended thiophene dimers (2Th1DT) were investigated by S. Yuan et al. reported in Scheme: 1.2.3.5 through DFT combined with nonequilibrium Green’s function energy level. The molecules are denoted a-i in scheme.
Rectification ratios were calculated to study the asymmetric properties of the current-voltage curves. The rectifying behavior in the 2Th1DT molecule including the amino group close to the molecular end was more important than that in the other molecules. The rectifying behavior was examined through transmission spectra and molecular projected self-consistent Hamiltonian states. Different heteroatoms were introduced into the 2Th1DT molecules to investigate the effect of heteroatoms e.g. C, N, O, S, Si and P on their electron transport properties. The computational results signified that the current in heteroatom containing molecules was larger than that in their pristine analogue, and lighter heteroatoms were more useful than heavier heteroatoms for electron transport of the thiophene dimer [170].
1.3 QUANTUM MECHANICAL BACKGROUND

1.3.1 THE SCHRÖDINGER EQUATION

Based on laws of quantum mechanics, the Schrödinger equation for the collection of quantum mechanical particles can be written in its generalized form as follows [171]:

$$\hat{H}\Psi(r) = E\Psi(r) \quad (1.3.1.1)$$

Where $\hat{H}$ is the Hamiltonian operator, $\Psi(r)$ is the wave function, and $E$ is a scalar quantity that stands for the energy of the system. There are number of formulations of this equation but the one referred to here is the time independent Schrödinger equation. The Hamiltonian operator of a system (in a.u) with $N$ electrons and $M$ nuclei is defined as

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{M} m_A \nabla_A^2 - \sum_{A=1}^{M} \sum_{i=1}^{N} \frac{Z_A}{r_{iA}} + \sum_{B=A}^{M} \sum_{A=1}^{M} \frac{Z_A Z_B}{R_{AB}} + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}} \quad (1.3.1.2)$$

Where $A$ and $B$ refer to $M$ nuclei and $i$ and $j$ refer to the $N$ electrons in the system. The first two term on the right hand side of equation 1.3.1.2 is a sum of differential operators, $\nabla^2$, which, when acting on the wave function $\Psi(r)$, produces the total kinetic energy of the electrons and nuclei respectively. The third term is the potential energy of the attractions between the electrons and nuclei. The fourth term is the potential energy of the repulsions between the nuclei. The last term is the potential energy of the repulsions between the electrons. $Z_A$ and $Z_B$ are the charges of respective nucleus, $r_{iA}$ is distance between the electron and nucleus $A$, $R_{AB}$ is the distance between nuclei $A$ and $B$ and $r_{ij}$ is distance between $i^{th}$ and $j^{th}$ electrons. An exact solution to the Schrödinger equation is possible only for trivial molecular systems; several simplifications are applied for solving the equation for larger molecules. For the practical purposes, some approximations are applied to solve the Schrödinger equation.

1.3.2 THE BORN-OPPENHEIMER APPROXIMATION

The approximation proposed by Born and Oppenheimer [172] was the first of several approximations used to simplify the solution of the Schrödinger equation. It simplifies the general molecule problem by separating nuclear and electronic motions. This approximation is reasonable since the mass of a nucleus is thousands times greater than that of an electron. The nuclei move very slowly with respect to the electrons, and the electrons react instantaneously to changes in nuclear position. Thus, the electron
distribution within a molecular system depends on the position of the nuclei, and not on their velocities. Put in a different way, electronic motion can be described as occurring in a field of fixed nuclei. The full Hamiltonian for the molecular system can also be written as

\[
H = T_{\text{elec}}(\vec{r}) + T_{\text{nucl}}(\vec{R}) + V_{\text{nucl-elec}}(\vec{R}, \vec{r}) + V_{\text{elec}}(\vec{r}) + V_{\text{nucl}}^{\text{int}}
\]  

(1.3.2.1)

The using Born-Oppenheimer Approximation, the electronic Hamiltonian \( H \) which separate kinetic energy term for the nuclei for the molecular system can be written as:

\[
H_{\text{elec}} = -\frac{1}{2} \sum_i T_{\text{elec}}^i + \sum_{ij} V_{\text{elec-elec}}(r_{ij}) + \sum_{ik} V_{\text{elec-nucl}}(r_{ik})
\]

(1.3.2.2)

1.3.3 BASIS FUNCTIONS AND BASIS SETS

A basis set is a mathematical description of an orbital within a system (which in turn combines to approximate the total electronic wave function) important for theoretical calculations [173-180]. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the location of electrons in space. A commonly used set of basis functions for Hartree-Fock calculations is the set of Slater type orbitals (STO) whose normalized form is

\[
\text{STO}_{nlm}(r, \theta, \phi) = \left( \frac{2\zeta}{a_0} \right)^{\frac{n+1}{2}} r^{n-\frac{1}{2}} e^{-\frac{r}{a_0}} Y_l^m(\theta, \phi)
\]

(1.3.3.1)

\( \zeta \) is orbital exponent, \( a_0 \) is Bohr’s radius, \( n, l \) and \( m \) are quantum numbers, \( Y_l^m \) is spherical harmonics. To simplify molecular integral evaluation, Boys proposed in 1950 the use of Gaussian-type functions (GTFs) instead of STO for the atomic orbitals in a linear combination atomic wave function. The GTF equation is

\[
g_{ijk} = N x_i^a y_j^a z_k^a e^{-ar^2}
\]

(1.3.3.2)

Where \( N \) is the normalization constant, \( \alpha \) is the positive orbital exponent, \( i, j, k \) are nonnegative integers.

When \( i + j + k = 0 \), i.e. \( i = 0, j = 0, k = 0 \), the GTF is called an s-type Gaussian.

When \( i + j + k = 1 \), then we have a p-type Gaussian which contains the factor \( x_a, y_a, z_a \).
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When \( i + j + k = 2 \), we have a d-type Gaussian. The GTF is better over STO since molecular integrals are calculated fast and it can be differentiated trivially any number of times in comparison to STO which is difficult to differentiate analytically and is time consuming to calculate molecular integrals.

There are three representative Gaussian functions (s, p, and d type respectively).

\[
g_x(\alpha, r) = \left( \frac{2\alpha}{\pi} \right)^{\frac{3}{2}} e^{-\alpha r^2} \quad (1.3.3.3)
\]

\[
g_y(\alpha, r) = \left( \frac{128\alpha^5}{\pi^3} \right)^{\frac{3}{4}} Y_4 e^{-\alpha r^2} \quad (1.3.3.4)
\]

\[
g_{x,y}(\alpha, r) = \left( \frac{2048\alpha^7}{\pi^3} \right)^{\frac{3}{4}} x y e^{-\alpha r^2} \quad (1.3.3.5)
\]

An alternative to Cartesian Gaussian functions is spherical Gaussians, whose real form is

\[
g_{nlm} = N r_n e^{-\alpha r^2} \left( \frac{Y_{l+}^m \pm Y_l^m}{2} \right) \quad (1.3.3.6)
\]

In Gaussian-basis-set terminology, instead of using the individual Gaussian function as basis functions, each basis function is taken as a linear combination of a small number of Gaussians, according to

\[
\chi_{\mu} = \sum_{\rho} d_{\mu,\rho} g_{\rho} \quad (1.3.3.7)
\]

Where \( \chi_{\mu} \) is called contracted Gaussians type function, \( d_{\mu,\rho}'s \) are fixed constants within a given basis set and \( g_{\rho}'s \) are called primitive Gaussians. All of these constructions result in the following expansion for the molecular orbitals.

\[
\phi_i = \sum_{\mu} C_{\mu,i} \chi_{\mu} = \sum C_{\mu} \left[ \sum_{\rho} d_{\mu,\rho} g_{\rho} \right] \quad (1.3.3.8)
\]

Thus, each STO is actually replaced by a linear combination of contracted Gaussian functions, which gives best fit to the optimized STO. These are called STO-NG basis set; ‘N’ is the number of primitive Gaussian functions used to fit an STO. Basis set generated from a sum of two Gaussian functions with different orbital exponents are called double zeta basis set. Only the valence orbitals are expressed by a double zeta representation in general. Basis set, which describes the inner shell electrons by a single contracted
Gaussian function and the valence shell electrons by a sum of Gaussian functions are referred as split-valence basis sets. Similarly if a basis set is having three contracted Gaussian functions per orbital, it is called triple zeta basis set (TZ). For example, consider 6-31G basis set. The 6 tells us that the each inner shell orbital is given by a sum of six primitive Gaussian functions. The hyphen indicates a split-valence basis set, which tells that the valence orbitals are represented by a pair of Gaussians.

Split valence basis sets allow change in the size of the orbitals but not the shape. This can be solved in the form of polarized basis set by adding orbitals with angular momentum beyond what is required for the description of each atom in the valence shell. Polarized basis sets adds d-functions to first and second row atoms and f-functions to transition metal elements indicated by 6-31G* or d in 6-31G(d) basis set notation. One asterisk (*) at the end of a basis set denotes that d functions are added to heavy atoms. Two asterisk (**) means that p functions are added to hydrogen atom in addition to the d functions on heavy atoms. Diffuse functions (with small orbital exponent value) allow orbitals to occupy a larger region of space and are important for systems where electrons are relatively far from the nucleus, molecules with lone pairs, anions and other systems with significant negative charge. Diffuse basis sets are represented by the ‘+’ signs. One ‘+’ means diffuse functions are added to heavy atoms while ‘++’ signals that diffuse functions are added to hydrogen atoms as well e.g. the 6-31+G* basis set is formed from the 6-31G* basis set with diffuse functions added to heavy atoms and 6-311++G* adds diffuse function to the hydrogen atom as well [181].

1.3.4 ELECTRON CORRELATION

The Hartree-Fock method gives "absolute" energies that are too high, because it overestimates electron-electron repulsion. There are two kinds of electron electron repulsion: classical Coulomb (Coulomb hole), arising from electric charge, and quantum mechanical or Fermi repulsion (Fermi hole), which exists between electrons of like spin. Coulomb hole is the space surrounding each electron where the probability of finding another electron is small. Thus, the motion of electrons is correlated with each other and is termed as electron correlation. Electron correlation is a term to describe the inadequacies of the Hartree-Fock model. In the Hartree-Fock model, the repulsion energy
between two electrons is calculated between an electron and the average electron density for the other electron. It doesn't take into account the fact that the electron will push away the other electrons as it moves around. This tendency for the electrons to stay apart diminishes the repulsion energy. Actually, one must consider the instantaneous interactions between electrons. Since electrons repel each other they tend to keep out of each other’s ways. For example, in helium, if one electron is close to nucleus at a given instant, it is energetically more favorable for the other electron to be far from nucleus at that instant.

Hartree-Fock wave function does have some instantaneous electron correlation built into it. A Hartree-Fock function satisfy the antisymmetry requirement of the Pauli principle therefore it vanishes when two electron with same spin have the same spatial coordinates. For a Hartree-Fock function, there is little probability of finding electron of the same spin in the same region of space, so a Hartree-Fock function has some correlation of the motions of electrons with the same region of space. This makes the Hartree-Fock energy is lower than the Hartree energy. But the motions of the electrons with opposite spin remain uncorrelated in Hartree-Fock wave function. The correlation energy is the difference between the exact non-relativistic energy $E_{\text{nonrel}}$ and the Hartree-Fock energy $E_{\text{HF}}$.

$$E_{\text{corr}} = E_{\text{nonrel}} - E_{\text{HF}} \quad (1.3.4.1)$$

Any method which treats this phenomenon in a proper way is known as electron correlation method. Two methods deal with electron correlation

1. Configuration interaction [182]
2. Mollner-Plesset Perturbation Theory [183-184]

1.3.5 DENSITY FUNCTIONAL THEORY (DFT)

DFT is a quantum mechanical theory to explore the electronic structures of numerous body system, in particular atoms, molecules and the condensed phase. The DFT approach is based upon an approach of modeling electron correlation via general functionals of the electron density. Such methods owe their modern origins to the Hohenberg-Kohn theorem which established the existence of a unique functional which determines the ground state energy and density exactly. Following the work of Kohn and
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Sham, the approximate functionals utilized by current DFT methods partition the electronic energy into several terms [185-186]:

\[ E = E^T + E^V + E^J + E^{XC} \]  \hspace{1cm} (1.3.5.1)

Where \( E^T \) is the kinetic energy term (arising from the motion of the electrons), \( E^V \) includes terms describing the potential energy of the nuclear-electron attraction and of the repulsion between pairs of nuclei, \( E^J \) is the electron-electron repulsion term (it is also described as the Coulomb self-interaction of the electron density) given in equation 1.3.5.2.

\[ E^J = \frac{1}{2} \int \int \rho(\vec{r}_i) (\Delta(\vec{r}_i))^{-1} \rho(\vec{r}_j) d\vec{r}_i d\vec{r}_j \]  \hspace{1cm} (1.3.5.2)

\( E^T + E^V + E^J \) corresponds to the classical energy of the charge distribution \( \rho \). The \( E^{XC} \) term accounts for the remaining terms in the energy:

1) Exchange energy arising from the antisymmetry of the quantum mechanical wave function
2) Dynamic correlation in the motion of the individual electrons.

The exchange correlation energy functional \( E^{XC} \) is divided into separate parts referred to as the exchange and correlation parts, but actually corresponding to same spin and mixed-spin interactions respectively.

\[ E^{XC}(\rho) = E^X(\rho) + E^C(\rho) \]  \hspace{1cm} (1.3.5.3)

All three terms are again functional of the electron density, and functional defining the two components on the right hand side of equation 1.3.5.3 are termed as exchange functional and correlation functional respectively.

Some commonly used exchange functional are Perdew and Wang’s 1986 functional (which contains no empirical parameters) designated as PW86, Becke’s 1988 functionals denoted B88, and Perdew and Wang’s 1991 exchange functional PW91. The PW86 functionals and B88 functionals work about equally well in predicting molecular properties. The others are LYP (Lee-Yang-Parr) functional, P86, B96. Most popular hybrid method is B3LYP [187-190]. It uses Becke’s three parameters exchange functional with Lee-Yang-Parr (LYP) correlation functional. This method is known to give better results for geometries than at MP2 level and often energetic comparable to
QCISD(T) level. Another familiar hybrid method is B3PW91 [191], which use Perdew correlation functional instead of LYP in B3LYP method.

### 1.3.6 MOLLER PLESSET PERTURBATION THEORY

While the configuration interaction method is clearly a rigorous way to add correlation to the Hartree-Fock results, the method is computationally very demanding because of the large number of excited slater determinants that need at least in principle to be included. Another commonly used estimate of the correlation energy is based on perturbation theory rather than variational calculations and is usually referred to as Moller-Plesset perturbation theory. Perturbation theory is a technique to acquire more accurate wave functions and energies by the successive perturbations of an idealized model system with known eigenstates and eigenvalues [183-184]. The Hamiltonian, \( \hat{H}^{(0)} \), ground state wave function, \( \Psi^{(0)} \), and ground state energy, \( E^{(0)} \), of the model system are said to be zeorth order. The counterparts for the real system can then be written

\[
\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}
\]

\[
\Psi = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \ldots
\]

\[
E = E^{(0)} + E^{(1)} + E^{(2)} + \ldots
\]

(1.3.6.1)

Where \( \hat{H}^{(1)} \) is the perturbation which leads to the Hamiltonian of the exact relativistic system while \( \Psi^{(i)} \) and \( E^{(i)} \) is the \( i \)th correction to the zeorth order wave function and energy, respectively. In Moller Plesset (MP) perturbation theory, \( \hat{H}^{(0)} \) is defined as the sum of one-electron Fock operators given in equation 1.3.6.1 while \( \Psi^{(0)} \) is the Slater determinant with HF optimized occupied MOs. For the model system, the zeorth order MP energy (MP\(_0\)) is given by the sum of the \( n \) occupied MO energies

\[
E_{MP0} = E^{(0)} = \langle \Psi_{HF} | H^{(0)} | \Psi_{HF} \rangle = \sum_j E_j
\]

(1.3.6.2)

The MP perturbation, which leads to the correct Hamiltonian, is given by

\[
\hat{H}^{(1)} = \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{1}{r_{ij}} - \sum_i v^{HF}(i)
\]

(1.3.6.3)

Where \( v^{HF}(i) \) is the HF potential felt by electron i.
\[ E_{MP1} = E^{(0)} + E^{(1)} \]
\[ = \langle \Psi_{HF} | H^{(0)} | \Psi_{HF} \rangle + \langle \Psi_{HF} | \hat{H}^{(1)} | \Psi_{HF} \rangle \]
\[ = \langle \Psi_{HF} | H^{(0)} + \hat{H}^{(1)} | \Psi_{HF} \rangle \]
\[ = E_{HF} \]

\( E^{(1)} \) is simply the correction that gives the HF energy. Thus, corrections to higher order are required to improve on HF. While the calculations of \( E_{MP0} \) and \( E_{MP1} \), only require the HF configuration, all higher order correction include excited state configurations. In particular, the second order MP correction to the energy is given by

\[ E^{(2)} = \sum_{J \neq HF} \frac{\langle \Psi_J | \hat{H}^{(1)} | \Psi_{HF} \rangle \langle \Psi_{HF} | \hat{H}^{(1)} | \Psi_J \rangle}{E^{(0)} - E_J} \]  

(1.3.6.5)

The MP2 energy is computed as \( E_{MP1} + E^{(2)} \). The sum in equation 1.3.6.5 formally runs over all excited configurations J.

### 1.3.7 NBO ANALYSIS

The NBO program [192-194] performs the analysis of many electron molecular wave functions in terms of localized electron pair units. The program carries out the determination of Natural Atomic Orbitals (NAOs), Natural Hybrid Orbitals (NHOs), Natural Bond Orbitals (NBOs) and Natural Localized Molecular Orbitals (NLMOs) and uses these to perform Natural Population Analysis (NPA). The NBO method makes use of only the first order reduced density matrix of the wave function and hence is applicable to wave function of general mathematical form, corresponding to the one centre (lone pair) and two centre (bond) elements of the chemists Lewis structure picture.

NBO analysis is based on a method for optimally transforming a given wave function into localized form. The various natural localized sets can be considered to result from a sequence of transformation of the input atomic orbital basis set (\( \xi_i \)).

Input basis → NAOs → NHOs → NBOs → NLMOs

The overlap associated with NAOs can be used to estimate the strength of orbital interactions in the usual way. The optimal condensation of occupancy in natural localized orbital leads to partitioning into high and low occupancy orbital types. Each pair of
valence hybrids $h_A$ and $h_B$ in the NHO basis set give rise to a bond ($\sigma_{AB}$) and antibond ($\sigma^*_{AB}$) in the NBO basis.

$$\sigma_{AB} = c_A h_A + c_B h_B$$

$$\sigma^*_{AB} = c_B h_A - c_A h_B$$

The former a Lewis (L) and the latter a non-Lewis (NL) orbital. The antibonds (valence shell non-Lewis orbitals) typically play the primary role in departures (delocalization) from the idealized Lewis structure.

The filled orbital of formal Lewis structure interacts with one of the unfilled antibonding orbitals to give the second stabilization order energy [$E^{(2)}$] which is given by:

$$E^{(2)} = \frac{-2F_{ij}}{\Delta E_{ij}}$$

Where $\Delta E_{ij}$ is the energy difference between interacting orbitals and $F_{ij}$ is the Fock matrix elements. The $E^{(2)}$ values quantify hyperconjugative interactions which can be estimated using NBO analysis. NBO is helpful in studying the delocalization of electrons in the compounds of interest in the research work [195]. The NBO program makes an extensive provision for energetic analysis of NBO interactions. Estimate of energy effects are based on second-order perturbation theory or on the effects of deleting certain orbitals or matrix element and recalculating the total energy. NBO analysis is also originated as a technique for studying hybridization and covalency effects in polyatomic wave functions. NBO has become a reliable tool for hydrogen bond analysis and is used to derive information on the changes in charge densities in the proton donor as well as changes in bonding and antibonding space. Charge transfer from lone pair of electron donor is mainly directed to antibonding orbitals in remote part of complex. The primary effect is accompanied with secondary effect of structural reorganization of the proton donor leading to contraction of A···H bond and blue shift in A-H frequency [196].

1.3.8 NEDA ANALYSIS

Contributions to NEDA include [197-199]:

1. Electrical (EL) component, considered to represent the classical-like columbic interactions between atomic charges, bond dipoles.
2. Steric exchange (EX) component, considered to represent Pauli exchange-type repulsion between filled orbitals.

3. Charge transfer (CT) component, considered to represent resonance-type “delocalization” interaction between filled orbitals of one subunit and unfilled orbitals of the other.

Thus EL component may be further divided into static (ES) and induced “polarization” (POL) components [with associated “self-energy” (SE) correction for the energetic penalty at each polarizing centre], and post-HF “correlation” (CORR) or other components may be added in more refined treatments.

The usual expression for the binding energy $\Delta E$ of the A···B complex is as follow:

$$\Delta E = E(\psi_{AB}) - [E(\psi_A) + E(\psi_B)]$$  \hspace{1cm} (1.3.8.1)

Where $\psi_{AB}$ is the wave function of the AB complex and $\psi_A$, $\psi_B$ are the wave functions for isolated A, B subunits. The $\Delta E$ is comprised of EL, CORE and CT components which may be abbreviated as

$$\Delta E = EL + CORE + CT$$  \hspace{1cm} (1.3.8.2)

All NEDA energy evaluations in equation 1.3.8.1 employ the full basis set of the complex, so that $\Delta E$ automatically incorporates the full Boys-Bernardi “counterpoise correction” for BSSE.

The key step of NEDA analysis is evaluation of perturbed wave functions $\psi_A^{(\text{def})}$, $\psi_B^{(\text{def})}$ for each monomer as local eigenvectors of the NBO Fock matrix in the respective monomer blocks. The antisymmetrized (determinantal) product of perturbed fragment wave functions then defines the starting “localized” ($\psi_{AB}^{(\text{loc})}$) wave function that underlies evaluation of each NEDA component.

$$\psi_{AB}^{(\text{loc})} = \det |\psi_A^{(\text{def})} \psi_B^{(\text{def})}|$$  \hspace{1cm} (1.3.8.3)

Consistent with its physical description as delocalization from each fragment into unfilled orbitals of the other, the CT component is defined directly as

$$CT = E(\psi_{AB}) - E(\psi_{AB}^{(\text{loc})})$$  \hspace{1cm} (1.3.8.4)

The energy difference between $\psi_A^{(\text{loc})}$ and the perturbed fragment wave functions $\psi_A^{(\text{def})}$, $\psi_B^{(\text{def})}$ is attributed to a sum of ES, POL and EX contributions

$$ES + POL + EX = E(\psi_{AB}^{(\text{loc})}) - [E(\psi_A^{(\text{def})}) + E(\psi_B^{(\text{def})})]$$  \hspace{1cm} (1.3.8.5)
The “deformation” energy (DEF) of forming each perturbed localized $\psi_A^{(\text{def})}$ from its starting fragment wave function $\psi_A$ is calculated in a similarly direct manner as corresponding to combined electric field and quantum mechanical effects experienced by each fragment within complex.

$$\text{DEF} = [E(\psi_A^{\text{def}}) - E(\psi_A)] + [E(\psi_B^{\text{def}}) - E(\psi_B)] \quad (1.3.8.6)$$

In accordance with electrodynamics, one can employ linear response theory to evaluate the self-energy (SE) correction (“polarization penalty”) for each centre, thereby expressing the total electrical component as

$$\text{EL} = \text{ES} + \text{POL} + \text{SE} \quad (1.3.8.7)$$

However, the self energy must then be removed (subtracted from the deformation (DEF) penalty to obtain the net repulsive CORE component

$$\text{CORE} = \text{EX} + \text{DEF} - \text{SE} \quad (1.3.8.8)$$

By combining the definitions for EL (equation 1.3.8.7), CORE (equation 1.3.8.8) and CT (equation 1.3.8.4), one readily verifies that these components satisfy the basic NEDA,

$$\Delta E = \text{ES} + \text{POL} + \text{EX} + \text{DEF} + \text{CT}$$

### 1.3.9 AIM ANALYSIS

AIM [200] allows us to study the bonding properties of the system, to examine the switches in bonding and to see whether the bonds are covalent or ionic. It is apparent that specific features of hydrogen bonding cannot be understood only in terms of intermolecular energy, but may also be computed using AIM theory. AIM theory is useful for exploring the influence of the crystal environment and intermolecular interactions. This incorporates the design and synthesis of new molecules and new materials with definite desirable properties. AIM theory methodology carry out numerical integration of electron density whereby a number of topological parameters, such as electron density ($\rho$) and the Laplacian ($\nabla^2 \rho$) descriptor are analyzed. According to Koch and Poplier, the characterization of intra- and/or intermolecular hydrogen bond interaction is based on bond critical point (BCP) located between neighboring atoms that must obey following important criteria [201-202]:
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1. Presence of BCP for the H···A contact which topologically proves the existence of hydrogen bonding interaction.
2. Value of electron density at the BCP of H···A lies within the range of 0.002-0.040 au.
3. The corresponding Laplacian of electron density at the BCP is 0.024-0.139 au.
4. There is mutual penetration of hydrogen and acceptor atom.
5. Decrease net charge of the hydrogen atom.
6. There is energetic destabilization of the hydrogen atom.
7. Decrease of dipolar polarization of the hydrogen atom.
8. Decrease of volume of the hydrogen atom.

The Bonded radius of an atom (r_b) and the Bond path Length

The distance of a BCP from nucleus A determines the “bonded radius” of atom A and is indicated by r_b(A). The bond path (BP) is a curve in real space linking two bonded nuclei along which \( \rho \) is a maximum with respect to any neighboring line. The BCP lies on the BP and therefore it adopts the property that defines the BP. If the bond path is coincident with the internuclear axis then the sum of the two associated bond radii termed the bond path length equal to bond length. If however the bond path is curved or strained chemically, the bond path length will exceed the bond length.

Critical Point

The analysis of critical points in the electron density seems to be most important for studies in interatomic interactions. These interactions may be connected with typical covalent bonds and with intermolecular nonbonded contacts such as hydrogen bonds.

Critical point in the electron density is a point in space at which the first derivative of the \( \rho \) vanishes.

\[
\nabla \rho = i \frac{d\rho}{dx} + j \frac{d\rho}{dy} + k \frac{d\rho}{dz} \rightarrow 0 \text{ (at critical points and at infinity)}
\]

Generally is not equal to zero at all other points. One can distinguish between a local minimum, a local maximum or a saddle point by considering the second derivatives, the element of the tensor \( \nabla \nabla \rho \). There are nine second derivatives of \( \rho(r) \) that can be arranged in the so-called “Hessian matrix” which when evaluated at a critical point located at \( r_c \) is written as
\[
A(r_c) = \begin{pmatrix}
\frac{\partial^2 \rho}{\partial x^2} & \frac{\partial^2 \rho}{\partial x \partial y} & \frac{\partial^2 \rho}{\partial x \partial z} \\
\frac{\partial^2 \rho}{\partial y \partial x} & \frac{\partial^2 \rho}{\partial y^2} & \frac{\partial^2 \rho}{\partial y \partial z} \\
\frac{\partial^2 \rho}{\partial z \partial x} & \frac{\partial^2 \rho}{\partial z \partial y} & \frac{\partial^2 \rho}{\partial z^2}
\end{pmatrix}
\] (1.3.9.1)

The diagonalization of \( A(r_c) \) is equivalent to a rotation of the coordinate system \( r(x, y, z) \)
\( \rightarrow r(x', y', z') \) superimposing the new axes \( x', y', z' \) with the principal curvature axes of
the critical point. The rotation of the coordinate system is accomplished via unitary
transformation, \( r' = rU \) where \( U \) is a unitary matrix constructed from a set of three
eigenvalue equations \( Au_i = \lambda_i u_i \) (\( i = 1, 2, 3 \)) in which \( u_i \) is the \( i \)-th column vector in \( U \). A
transformation \( U^{-1}AU = \Lambda \) transform the Hessian into its diagonal form, which is written
explicitly as:

\[
\Lambda = \begin{pmatrix}
\frac{\partial^2 \rho}{\partial x'^2} & 0 & 0 \\
0 & \frac{\partial^2 \rho}{\partial y'^2} & 0 \\
0 & 0 & \frac{\partial^2 \rho}{\partial z'^2}
\end{pmatrix}
\] = \begin{pmatrix}
\lambda_1 & 0 & 0 \\
0 & \lambda_2 & 0 \\
0 & 0 & \lambda_3
\end{pmatrix}
\] (1.3.9.2)

In which \( \lambda_1, \lambda_2 \) and \( \lambda_3 \) are the curvatures of the density with respect to the three principal
axes \( x', y', z' \). Stable critical points fall into four categories having three non-zero eigen
values:

1. (3, -1) Bond critical point (BCP), \( \rho \) is maximum in the plane defined by
corresponding eigenvectors but is minimum along the third axis which is
perpendicular to this plane. When computed for the charge density, this path so form
is called bond path which connects two atoms.

2. (3, +1) Ring critical point (RCP), \( \rho \) is minimum in the plane defined by corresponding
eigenvectors but is maximum along the third axis which is perpendicular to this plane.

3. (3, -3) Nuclear critical point (NCP), \( \rho \) is maximum.

4. (3, +3) Cage critical point (CCP), \( \rho \) is minimum.

Several properties evaluated at the BCP summarize the characteristics of the
corresponding bond. The electron density at the BCP denoted by \( \rho \) determines a bond
order and strong correlations have been found between bond energy and \( \rho \). There are
several reports in the literature that illustrate that $\rho$ at BCP and hydrogen bond distance exhibit a linear relationship.

**Laplacian of the electron density at the BCP ($\nabla^2 \rho$)**

Laplacian identifies regions of space where the electron charge is locally depleted or concentrated. An important property of the Hessian is that its trace is invariant to rotations of coordinate system. The trace of the Hessian of the density is recognized as the Laplacian of the density $[\nabla^2 \rho(r)]$, when $x = x'$, $y = y'$ and $z = z'$ using equation 1.3.9.2 is written as

$$\nabla^2 \rho(r) = \nabla \cdot \nabla \rho(r) = \frac{\partial^2 \rho(r)}{\partial x^2} + \frac{\partial^2 \rho(r)}{\partial y^2} + \frac{\partial^2 \rho(r)}{\partial z^2}$$

(1.3.9.3)

Where $\frac{\partial^2 \rho(r)}{\partial x^2} = \lambda_1$, $\frac{\partial^2 \rho(r)}{\partial y^2} = \lambda_2$, $\frac{\partial^2 \rho(r)}{\partial z^2} = \lambda_3$

The $\nabla^2 \rho$ at the BCPs differentiate two broad classes of bond

1. if $\nabla^2 \rho < 0$, the bond is called shared interaction.
2. if $\nabla^2 \rho > 0$, the bond is called closed shell interaction.

Covalent bonds belong to former class for e.g. $\nabla^2 \rho = -1.1$ au for a typical C-H bond. In contrast, in closed shell bonding, for e.g. ionic bonds, hydrogen bond or van der Waals interactions are described by a depletion of density in the region of the two atoms.

**The Electron density at the BCP ($\rho$)**

The strength of chemical bond, its bond order (BO) is reflected in the electron density at the BCP ($\rho$)

$$\text{BO} = \exp[A (\rho-B)]$$

(1.3.9.4)

Where $A$ and $B$ are constants which depends on the nature of the bonded atoms. In general $\rho$ is greater than 0.20 au in shared (covalent) bonding and less than 0.10 au in a closed shell interaction. The electron density increases with the hydrogen bond strength and hence gives useful information about the strength of bond.

### 1.4 METHODOLOGY TO CALCULATE VARIOUS PROPERTIES

#### 1.4.1 STABILIZATION ENERGIES

A supersystem refers to a system by noncovalent interactions between two or more molecular entities e.g. hydrogen bond systems. The stabilization energy (S.E.) of
such a system is calculated as difference between energy of supersystem and sum of energies of its subsystem using expression 1.4.1.1

\[ S.E. = E_{AB} - [E_A + E_B] \]  \hspace{1cm} (1.4.1.1)

Where \(E_{AB}\) is the electronic energy of supersystem, \(E_A\) and \(E_B\) refer to energies of subsystem.

The adduct formation is accompanied by structural distortion and distortion energies \((E_{\text{Dis}})\) estimates energy change accompanying distortion that are calculated using equation 1.4.1.2

\[ E_{\text{Dis}} = (E_{a,\text{Dis}} + E_{b,\text{Dis}}) - (E_a + E_b) \]  \hspace{1cm} (1.4.1.2)

Where \(E_a\) and \(E_b\) are the energies of fully optimized individual monomers, \(E_{a,\text{Dis}}\) and \(E_{b,\text{Dis}}\) are single point energies obtained for the distorted monomeric geometry present in the adduct [203].

**CORRECTION FOR BASIS SET INCOMPLETENESS**

In studies of weakly bound clusters, one often encounters an artificial shortening of intermolecular distances and concomitant artificial strengthening of the intermolecular interaction. Such problems are ascribed to “basis set superposition errors” (BSSEs) and they are more pronounced for smaller basis sets. As monomer A approaches monomer B, the dimer can be artificially stabilized as monomer A utilizes the extra basis functions from monomer B to describe its electron distribution, and vice versa. Origin of BSSE lies in possibility that the unused basis function of monomer B in associated complex may enlarge the basis set of monomer A, thereby lowering its energy compared to calculation of this unit alone. An approximate way of accessing BSSE is counterpoise (CP) correction method introduced by Boys and Bernardi in which the BSSE can be estimated as the difference between monomer energies with the regular basis and the energies calculated with full set of basis functions for dimer [204-205]. The CP method estimate each of the unit with just the basis functions of other (without the nuclei or electron) using so called “ghost orbitals”.

**1.4.2 PROTON AFFINITY**

The proton affinity (PA) [206] of base B is defined as the negative of the enthalpy change \((\Delta H^{298})\) of the process in equation (Eq (1.4.2.1)).
B(g) + H⁺(g) → BH⁺(g)  \hspace{2cm} (1.4.2.1)

\[ \Delta H^{298} = H^{298}(BH^+) - H^{298}(B) - H^{298}(H^+) \]  \hspace{2cm} (1.4.2.2)

PA = -\Delta H^{298} = - [(E_e(BH^-) + ZPE(BH^-) + H_{vib}(BH^-)) - (E_e(B) + ZPE(B) + H_{vib}(B))] + 5/2RT  \hspace{2cm} (1.4.2.3)

Where \( E_e \) is the electronic energy, \( ZPE \) is zero point vibrational energy correction, \( H_{vib} \) is the vibrational enthalpy correction and the constant 5/2RT includes PV = RT (1 mole of gas) and translational energy (3/2RT) of the proton at 298.15 K. This shows negative of \( \Delta H^{298} \) includes change in total energy, in \( ZPE \), vibrational energy in going from 0 to 298.15 K and rotational and translational energy, and work term (RT).

1.4.3 GAS PHASE ACIDITY/DEPROTONATION AFFINITY

The gas-phase acidity [207] is defined as the enthalpy change of deprotonation (\( \Delta H^{298} \)) for Eq (1.4.3.1).

\[ AH(g) \rightarrow A^-(g) + H^+(g) \]  \hspace{2cm} (1.4.3.1)

The enthalpy of deprotonation, \( \Delta H^{298} \), was computed using equations 1.4.3.2 and 1.4.3.3.

\[ \Delta H^{298} = \Delta E^{298} + PV \]  \hspace{2cm} (1.4.3.2)

\[ \Delta E^{298} = E^{298}(A^-) + 3/2RT - E^{298}(AH) \]  \hspace{2cm} (1.4.3.3)

Where \( E^{298}(AH) \) and \( E^{298}(A^-) \) stand for the electronic energies of the acids and their anions (including the thermal energy correction at \( T = 298.15 \) K). In equation 1.4.3.2, we substituted PV = RT (1 mole of gas).

1.4.4 HYDRIDE TRANSFER

The hydride donor ability [208] of BH is defined as enthalpy change (\( \Delta H \)) of the process in equation 1.4.4.2

\[ BH(g) \rightarrow B^+(g) + H(g) \]  \hspace{2cm} (1.4.4.1)

\[ \Delta H^{298} = H^{298}(B^+) + H^{298}(H^-) - H^{298}(BH) \]  \hspace{2cm} (1.4.4.2)

\[ \Delta H^{298} = [(E_e(B^+) + E_e(H^-) + ZPE(B^+) + H_{vib}(B^+)) - (E_e(BH) + ZPE(BH) + H_{vib}(BH))] + 5/2RT \]  \hspace{2cm} (1.4.4.3)
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Where $E_e$ is the electronic energy, $ZPE$ is zero point vibrational energy correction, $H_{vib}$ is the vibrational enthalpy correction applied. The term $5/2RT$ includes $PV = RT$ (1 mole of gas) for above reaction and translational energy of the hydride ion.

1.4.5 BOND DISSOCIATION ENTHALPY (BDE)

The strength of a chemical bond expressed in terms of its BDE, is of fundamental importance in any consideration of chemical reactivity. The BDE is calculated as the enthalpy change of the following reaction in the gas phase at 298 K and 1 atm pressure.

$$\text{A-B(g)} \rightarrow \text{A'(g)} + \text{B(g)} \quad (1.4.5.1)$$

The BDE is defined as the sum of enthalpy of formation ($H_{f}^{298}$) of the products (radicals) minus those of reactants [209-210]

$$\text{BDE} = \Delta H_{f}^{298} = H_{f}(\text{A'}) + H_{f}(\text{B'}) - H_{f}(\text{A-B}) \quad (1.4.5.2)$$

The BDE has been calculated by using the following equation [211-214]

$$\Delta H_{f}^{298} = \Delta E_{e} + \Delta ZPE + \Delta H_{\text{trans}} + \Delta H_{\text{rot}} + \Delta H_{\text{vib}} + RT \quad (1.4.5.3)$$

Where $E_e$ is electronic energy, $ZPE$ is zero point vibrational energy, $H_{\text{trans}}$ is translational enthalpy, $H_{\text{rot}}$ is rotational enthalpy, $H_{\text{vib}}$ is vibrational enthalpy [215-216] of the molecule and $RT$ (PV work term) is the conversion factor from energy to enthalpy.

1.4.6 IONIZATION POTENTIAL (IP)

Ionization potential is easily accessible by computing the energy difference between the neutral molecule ($N$ electrons) and its radical cation ($N-1$ electrons). It is an endothermic process that absorbs energy. This property can only be measured in an atom in gaseous state using equation 1.4.6.1

$$\text{X} \rightarrow \text{X}^+ + \text{e}^-$$

$$\text{IP} = \text{E}_{\text{cation}} - \text{E}_{\text{neutral}} \quad (1.4.6.1)$$

The geometry of the radical cation can be quite different from that of the neutral, which leads to an energetic separation between the adiabatic and vertical IPs. While the energy difference based on a full geometry optimization of both species gives the adiabatic IP, ignoring the geometry change upon ionization (which is achieved through a single-point energy calculation on the geometrical structure of the neutral for ($N$-1) electrons) gives the vertical ionization potential [217].
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