IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

THEORETICAL STUDIES OF THE BARRIER TO INTERNAL ROTATION IN HYDROGEN PEROXIDE, HYDRAZINE AND ETHANE MOLECULES

Ajay Kumar
Department of Chemistry,
D. B. S. (PG) College Dehradun, Dehradun, Uttarakhand 248001, India

Abstract: The barrier to internal rotation in hydrogen peroxide (H_2O_2), hydrazine (NH_2NH_2) and ethane (C_2H_6) are calculated using ab-initio and semi-empirical MNDO methods and compared with experimental results. The MNDO barriers are seen to be too low and in the case of hydrogen peroxide and hydrazine only one barrier is obtained. The ab-initio values using minimal basis STO-3G calculations are satisfactory for ethane, but in hydrogen peroxide and hydrazine reasonable results are obtained only on using split valence or double-zeta basis including polarization functions.

Keywords: hydrogen peroxide (H_2O_2), hydrazine (NH_2NH_2) and ethane (C_2H_6), MNDO, molecular orbitals

I. INTRODUCTION

The notation of chemical structure is defined within the Born-Oppenheimer Approximation [1]. This approximation is fundamental to the theoretical treatment of molecular structure as it enable us to separate the nuclear and electronic motions. For a system consisting of v′ nuclei of charge Z_α (where α varies from 1 to v′) and n′ electrons, Hamiltonian equation be able to written (in atomic units) like,

$$H_a = -\frac{1}{2}\sum_{\alpha}\frac{1}{M_\alpha}\nabla_\alpha^{2} - \frac{1}{2}\sum_{i=1}^{n'}\nabla_i^2 - \sum_{\alpha=1}^{n'}\sum_{i=1}^{n'}\frac{Z_\alpha}{r_{i\alpha}} + \sum_{i=1}^{n'}\sum_{j>i}^{v}\frac{1}{r_{ij}} + \sum_{\alpha=1}^{v'}\sum_{\alpha>\beta}\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \text{ ------------ (1)}$$

$H_a = T_{n'} + T_e + V_{n'e} + V_{ee} + V_{n'm}$

Where the mass of nucleus is M_α and unit of m_e is α. In the Hamiltonian equation the first part represents the nuclei kinetic energy; the second part for electron kinetic energy; third is the nucleus-electron attraction potential energy; fourth part for the electron-electron repulsion and the fifth part for inter nuclear repulsion. To separate the electronic motion and nuclear we make use of the information that the nuclei are several orders magnitude bulkier than the electrons and therefore electronic motion will instantaneously adjust itself to any change in nuclear coordinates which take place. Thus we write the total wave function

$$\psi = \psi_n \psi_e \text{ -- (2)}$$

Where ψ_e depends on upon co-ordinates only parametrically. We solve the electronic eigen value problem.

$$H_e\psi_e = E_e\psi_e \text{ -- (3)}$$

Where H_e contains all the terms in the Hamiltonian except the nuclear kinetic energy terms. This procedure is followed for different rates of nuclear co-ordinates to yield the electronic energy ψ_e as a function of nuclear co-ordinates and the nuclear motion is then described by the equation.

$$(T_n + E_e)\psi_n = E\psi_n \text{ --- (4)}$$

That is the electronic energy may be considered as the function of potential energy use the problem of nuclear motion. Within this approximation stable chemical structures arise corresponding to the minima on the potential energy hyper surface defined the $E_e(R)$ (where R stands for set of all relevant nuclear co-ordinates).

The potential surface so defined is of fundamental significance to the theoretical study of molecular structure as well as dynamics. In computational practice locating the minimum in the potential energy surface at that point the equilibrium geometries of molecules are obtained. However, in the case of a reaction, the reactants and products corresponds to minima of and the Born-Oppenheimer potential energy surface constructed taking into account the coordinated of all atoms of the reacting species. The reaction coordinate correspond to a low energy path joining these minima or “Valleys” representing reactants and products, whereas the transition state corresponds to “Saddle Points” on the potential energy surface or the “Pass” between the “Valleys” and the energy change in the reaction correspond to the difference in energy between the reactants and products.

In the case of some molecular system a special situation arise where there are several “Valleys” or minima in the potential energy surface corresponding to essentially equivalent but different nuclear configuration having equal or almost equal energy being separated from one another by barriers of low heights or “Passes” which are easily accessible.

These facilities the easy inter conversion between nuclear configurations thermally. For each nuclear configuration the total electronic energy is usually calculated using a molecular orbital method.

MOLECULAR ORBITAL METHOD

In the molecular orbital (MO) method the molecular electronic wave function was build up from one electron functions or orbitals. In this the MO method is the exact analogue of the AO method. For atoms the wave function is constructed out of atomic orbital and for molecules out of molecular orbitals. Since electrons are Fermions, the many electron wave functions have to be anti symmetric with respect to interchange of electron coordinates. This is easily satisfied by writing the N-electron wave function in the form of a Slater determinant.

$$\bar{\psi}(1,2,.....N)=\frac{1}{\sqrt{N!}}\begin{bmatrix} v_1(1)v_1(2)v_1(3)................ & v_1(N) \\ v_2(1)v_2(2)v_2(3)................ & v_2(N) \\ . \quad . \quad . & . \\ . \quad . \quad . & . \\ v_n(1)v_{n1}(2)v_n(3)................ & v_n(N) \end{bmatrix} \text{------------------------------------} (5)$$

Here the $v_{i's}$ are spin orbitals and the factor $\frac{1}{\sqrt{N!}}$ takes care of the normalization requirement. If any two spin orbitals among the N are identical the determinant reduces to zero and this leads to the Pauli Exclusion Principle: no two orbitals in the set may be identical in both the space and spin parts. A wave function thus constructed is the minimum acceptable one in theory. The assignment of N electrons to the N spin orbitals gives rise to a ‘configuration’.

In the Hartree-Fock method we seek the best single determinantal (or single configuration) wave function or the optional set of orbitals that minimize the energy expectation values.

$$<H>=\frac{<\psi/H/\psi>}{<\psi \ /\psi>} \text{---} (6)$$

For a good number of systems there are even numbers of electrons and they may be assigned to N/2 distinct (space) orbitals with α and β spins. When we completed this we have the restricted Hartree-Fock method and this is satisfactory for closed shell cases. The RHF wave function be written as

$$\bar{\psi}(1,2,\ldots\ldots N)=\frac{1}{\sqrt{N!}}\begin{bmatrix} \phi_1(1) & \phi_1(2) & \phi_1(3)\ldots\ldots\ldots\ldots\ldots\phi_1(N) \\ \phi^{-}{}_1(1) & \phi^{-}{}_1(2) & \phi^{-}{}_1(3)\ldots\ldots\ldots\ldots\phi^{-}{}_1(N) \\ . & . & . \qquad\qquad . \\ . & . & . \qquad\qquad . \\ \multicolumn{3}{l}{\phi_{N/2}(1)\phi_{nN/2}(2)\phi_{N/2}(3)\ldots\ldots\ldots\ldots\ldots\phi_{N/2}(N)} \\ \multicolumn{3}{l}{\bar{\phi}_{N/2}(1)\bar{\phi}_{nN/2}(2)\bar{\phi}_{N/2}(3)\ldots\ldots\ldots\ldots\bar{\phi}_{N/2}(N)} \end{bmatrix} \text{------------------------- (7)}$$

Where the pair of orbitals Φ_i and $\bar{\phi}_i$ have the same space part and have α and β spin respectively.

Molecular orbitals are usually constructed as liner combinations of atomic orbitals (LCAO). However, it is current computational practice to seek them as a liner combination of a set of basis functions chosen to best represent the MO's with the available computational resource in mind. These basis functions may be used to construct the best AO's in an atomic Hartree-Fock calculation and then these used build MO's from or directly linearly combined to get the MO's. The quality of the results are determined by our choice of basis sets; the larger the basis the more flexibility we have, and the better results. This however is to be balanced against the computational time requirements, the time need increase very fast with basis size (approximately of the order of n^4). A large amount of effort has gone into the choice of basis sets, and several good basis sets for most of the lighter atoms are available in the literature [3].

The basis functions are usually chosen to be the form

$$u_{i,A} = (\text{spherical harmonic}) \times r_A^{n-1}\, e^{\xi_i r_A} \text{ --- (8)}$$

where r_A is the distance of the point from the nucleus A. These functions are called Slater type orbitals or STO's. A minimal basis set for a given atom includes are STO for n =1, four for n = 2 (one s and 3p's) etc. upto the highest occupied atomic shell in the atomic ground state. Thus a minimal basis for the water molecule will use one STO per H atom and five (1s, 2s and 2p) for the oxygen, a total of seven basis functions. We get much better results using a double-zeta basis set, where corresponding to each AO we use two STO's with differing ξ values. Anything higher than this is referred to as an extended basis. However, evolution of the necessary integrals is too laborious when using STO's and for a while Gaussian basis sets [3-4] consisting of functions of the type was vague.

$$X = x^n(1)\, y^n(2)\, z^n(3)\, e^{-\alpha r_A^2} \text{ -- (9)}$$

However, they have the wrong cusp behavior, as the Slater type 1s orbital has a non zero slope at r = 0 whereas the Gaussian has zero slope. Also we need a very large set of Gaussian to get reasonable results. Hence, it is the current practice to expand STO's in fixed combinations of GTO's and use them as basis functions, or to choose a contracted Gaussian basis where a number of Gaussian are combined into smaller number of liner combination by careful optimization (without any attempt to simulate the STO's). The notation STO-nG was introduced by Pople and Coworkers [2] to denote a minimal basis calculation with each STO expanded in terms of n Gaussian. Once the set of basis functions is chosen we proceed iteratively to determine the best single configuration wave function using the Roothaan-Hartree Fock equation [4-5].

Each orbital u_i is written as the liner combination of basis function Φ; and the ground state of the system is written as a single Slater determinant (Equation 7).

$$u_i = \sum_{p=1}^{m} C_{ip}\, \phi_p \text{ -- (10)}$$

The system Hamiltonian is partitioned into one electron and two electron parts.

$$\bar{H} = \sum_{i=1}^{N} \bar{H}_{(i)} + \sum_{i<j}\sum_{j=1}^{N} \frac{1}{r_{ij}} \text{ --- (11)}$$

Where $\bar{H}_{(i)}$ is the one electron operator

$$\bar{H}_i = -\frac{1}{2}\nabla_i^{\,2} - \sum_{\alpha=1}^{\nu}\frac{Z_\alpha}{R_{i\alpha}} \tag{12}$$

The total system energy has been shown to be

$$E = 2\sum_{i=1}^{N/2}\bar{H}_{(i)} + \sum_{i}^{N/2}\sum_{j}^{N/2}(2J_{ij} - K_{ij}) \tag{13}$$

where H_i, J_{ij} and K_{ij} are defined as

$$H_i = < u_i(1)\left|\bar{H}(1)\right|\psi_i(1) > \tag{14}$$

$$J_{ij} = < u_i(1)u_j(2)\left|\frac{1}{r_{12}}\right|u_i(1)u_j(2) > \tag{15}$$

$$K_{ij} = < u_i(1)u_j(2)\left|\frac{1}{r_{12}}\right|u_i(2)u_j(1) > \tag{16}$$

Then the u_i is the solutions to the pseudo-eigen value equation (17), since F itself depends on the u_i (and have the coefficients c_{ip}). This system then needs to be solved it relatively with a starting set of c_{ip}'s (and u_i's) being referred successively to get the self consistency criterion satisfied.

$$\bar{F}_{ui} = \varepsilon_i u_i \tag{17}$$

where the operator $\bar{F}$ is defined by

$$\bar{F} = \bar{H} + \sum_{j=1}^{N/2}(2\bar{J}_i - \bar{K}_i) \tag{18}$$

Where $\bar{J}_i$, $\bar{K}_i$ are defined through

$$< u_i\left|\bar{J}_i\right|u_i > = J_{ij} \tag{19}$$

$$< u_i\left|\bar{K}_i\right|u_i > = K_{ij} \tag{20}$$

The orbital energies are given by

$$\varepsilon_i = H_i + \sum_{i=1}^{N/2}(2J_{ij} - K_{ij}) \tag{21}$$

$$E = \sum_{i=1}^{n}(H_i + \varepsilon_i) \tag{22}$$

The calculation requires, therefore the assessment of several one and two electron integrals over the basis functions. When have an ab-initio method. In contrast approximate method like MNDO [6] use various approximates to some of the integrals and some parameters are empirically chosen to fit experimental data.

Also, in MNDO and other similar method only the valance electrons are explicitly treated. The valance shells molecular orbitals (ψ_i) are correspond to by liner combination of minimum basis of valence shell atomic orbitals (ϕ_ν);

$$\psi_i = \sum_{\nu} C_{\nu i}\,\phi_\nu \tag{23}$$

The coefficient $C_{\nu i}$ is established from Roothaan-Hall equation, which were assumed in the form of NDDO approximation such as,

$$\sum_{\nu}(F_{\mu\nu}-E_i\,\delta_{\mu\nu})C_{\nu i}=0 \text{ -- (24)}$$

Where, eigen value of the MO ψ_i is E_i and $\delta_{\mu\nu}$ the kronecher δ. The elements $F_{\mu\nu}$ of the Fock matrix are the sum of a one electron part $H_{\mu\nu}$, a two electron part and the electronic energy E_{el} is given by

$$H=\frac{1}{2}\sum_{\mu}\ \sum_{\mu}P_{\mu\nu}(H_{\mu\nu}+F_{\mu\nu}) \text{ -- (25)}$$

Where $P_{\mu\nu}$ is an element of the bond order matrix. It is assumed that the AO's φ_λ and φ_σ at atom B (A ≠ B). In this notation the NDDO Fock matrix elements are

$$F_{\mu\mu}=U_{\mu\mu}+\sum_{B}V_{\mu\mu}\,B+[(\mu\mu,\nu\nu)-\frac{1}{2}(\mu\mu,\nu\nu)]+\sum_{B}\ \sum_{\lambda,\sigma}^{B}P_{\lambda\sigma}\,(\mu\mu,\lambda\sigma) \text{ -------------------- (26)}$$

$$F_{\mu\nu}=\sum_{B}V_{\mu\nu}\,B+\frac{1}{2}P_{\mu\nu}[3(\mu\mu,\nu\nu)-(\mu\mu,\nu\nu)]+\sum_{B}\ \sum_{\lambda,\sigma}^{B}P_{\lambda\sigma}\,(\mu\mu,\lambda\sigma) \text{ -------------------- (27)}$$

$$F_{\mu\lambda}=B_{\mu\lambda}-\frac{1}{2}\sum^{A}\ \sum^{B}P_{\nu}\,(\mu\mu,\lambda\sigma) \text{ -- (28)}$$

The total energy E_{tot}^{mol} of the molecule is the sum of the electronic energy E_{el} and repulsion E_{AB}^{core} between the cores of atom A and B.

$$E_{tot}^{mol}=E_{el}+\sum_{A}\ <\sum_{B}E_{AB}^{core} \text{ -- (29)}$$

The heat of formation H_f^{mol} of the molecule is obtained from its total energy by subtracting the electronic energies E_{el}^{A} and adding the experimental heats of formation ΔH_f^{A} of the atom in molecule

$$H_f^{mol}=E_{tot}^{mol}-\sum_{A}E_{el}^{A}+\sum_{A}\Delta H_f^{A} \text{ -- (30)}$$

The electronic energies of the atom are calculated from restricted single-determinantal wave function using the same approximations and parameters as in molecular NDDO calculations. In the present work we have calculated the barriers to internal rotation in the molecules using MNDO and ab-initio methods using several basis sets.

II. SURVEY OF BARRIER CALCULATIONS

In Hydrogen peroxide, Hydrazine and ethane:

The cis and trans barriers to internal rotation in hydrogen peroxide have been accurately determined within the Hartree–Fock approximation using a [4s3pld/2slp] basis set and The effects of geometry optimization and polarization functions were also studied by T. H. Dunning, Jr. [7]. Lingchun Song et. al. employed the modern ab initio valence bond (VB) method for hydrogen peroxide and hydrazine to quantitatively investigate the torsional energy curves in terms of hyperconjugative stabilization, steric repulsion, and structural and electronic relaxations [8].

The barrier to internal rotation in molecule is calculated theoretically as the difference between the total energies of the molecule in two different conformations. The energies are very large in comparison to their difference or the barrier height. Hence, it must be expected that the result not be in good agreement with experiment. The first barrier to be calculated ab-initio was that in ethane by Pitzer and Lipscomb [9], using a minimal basis they found energies of -78.99155 and -78.99593 Hartree for the staggered and eclipsed configuration respectively. This gives a barrier of 0.00522 Hartree which corresponds to 3.3 kcal/mol, which was in surprisingly good agreement with the experimental estimate of 3.0 kcal/mol [10]. Clementi and Davis using Gussian basis sets obtained values between 0.00555 and 0.00606 Hartree (3.48 and 3.80 kcal/mol) for different basis sets [11]. Pedersen and Morokuma [12] obtained barrier of 2.88 kcal/mol using a medium sized Gaussian basis sets. Stewens obtained the value of 3.33 kcal/mol using different basis sets [13].

The MNDO calculations of Dewar and coworkers [6] gave a value of 1.0 kcal/mol the best experimental estimate available to data is that of Weiss and Leroi [14] who place the value at 2.98 kcal/mol.

The barriers in hydrogen peroxide have on the other hand been very difficult to reproduce in the early calculations surveyed by Kaldor and Shavitt [15]. Experimentally the equilibrium geometry of hydrogen peroxide is known to be non planer with the dihedral angle of 111.5° [16].

Experimentally the *cis* form lies 7.6 kcal/mol and trans form 1.1 kcal/mol above the equilibrium value. Kaldor and Shavitt in their SCF MO calculation [15] varied the dihedral angle with fixed inter nuclear distance and bond angle and found the *trans* form to be stables. Thus they obtained a *cis* barrier of 9.4 kcal/mol but no *trans* barrier. It was suspected that correlation effects may be very significant in this case. A *cis* barrier was first obtained by Fink and Allen [17]. Their values were 13.2 kcal/mol and 0.3 kcal/mol for the *cis* and *trans* barrier respectively, the *cis* barrier being a serious over estimate and the *trans* barrier an under estimate. The key to the H_2O_2 conundrum however, lay in geometry optimization. Dunning and Winter [18] with full geometry optimization obtained a *cis* barrier of 1.1 kcal/mol and trans barrier of 8.35 kcal/mol. The *cis* barrier being in excellent agreement with experiment and the trans barrier being over estimated by about 10 % several semi empirical calculation have also been made with no successes in reproducing the *cis* barrier. The MNDO studies of Dewar and Thiel [20] also involved geometry optimization but gave no *cis* barrier.

In comparison to ethane and hydrogen peroxide there have been very few calculations on hydrazine. Experimentally the equilibrium geometry is thought to have an angle of approximately 90° between the bisector planes of the two NH_2 groups [19]. Pedersen and Morokuma [10] obtained barriers of 11.05 kcal/mol at 0° and 6.21 kcal/mol at 180°, inter group angle, while using other geometry parameters at fixed values. The experimental barriers value available is somewhat doubtful at 3.14 kcal/mol. The MNDO study of Dewar predicted the stable configuration to be *trans* and the *cis* barrier to be about 8.0 kcal/mol. In this chapter reports the result of our studies of the barriers in these three systems.

III. RESULTS AND DISCUSSION

The calculations on the molecules of hydrogen peroxide (H_2O_2), hydrazine (NH_2NH_2) and ethane (CH_3CH_3) were performed on an IBM PC compatible machine with a Pentium processor. The MNDO calculations were performed using the program developed by Thiel [20]. The ab-initio calculations were performed using the micromole program of Handy and coworkers [21].

The MNDO calculations on these molecules were performed at various values of the dihedral angle with all the other geometrical parameters being optimized for each value of the dihedral angle. The variations of the orbital energies with dihedral angle are shown in Fig. 1.

The total energy and calculated heats of formation are shown in Fig. 2 and Fig. 3 respectively. The qualitative forms of both the curves are the same with a flat minimum near 180° (*trans*). When we attempt a total geometry optimization starting with a dihedral angle of 140° or 150° the optimum structure given by the program corresponded to the dihedral angle of 144° or 147° respectively. However, the total energies were in between those for *cis* and *trans* structures. The results of these optimization studies are given in Table-1. The minima identified by the program are probably to the fact that the energy was very slowly varying with dihedral angles at the starting values and so the steepest descent algorithm almost neglects the corresponding direction of geometry change. It also be noted that starting from the *cis* configuration we have a find structure which is nearly *cis* so that our argument above seems quite plausible, since near the maximum also the curve has zero slop.

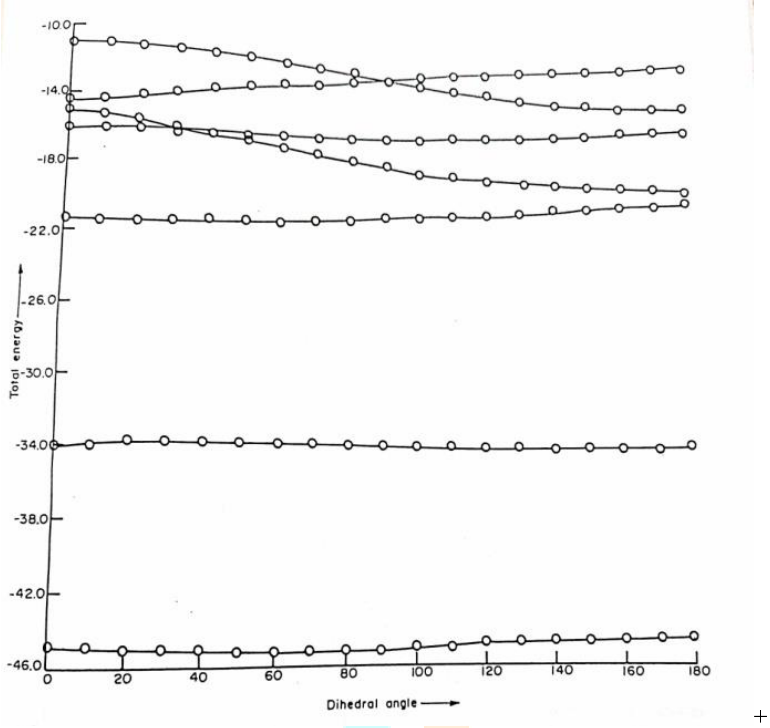

Fig. 1: MNDO MO energies as a function of dihedral angle in hydrogen peroxide.

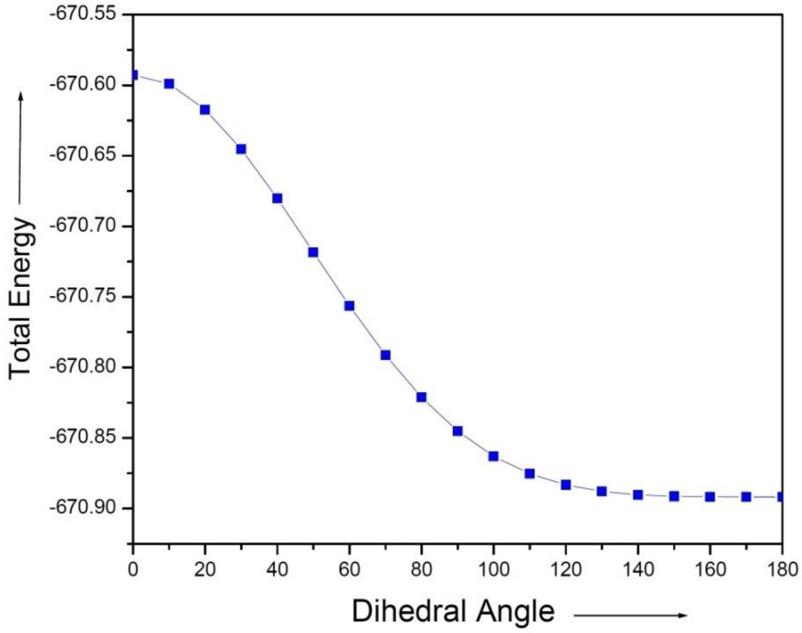

Fig. 2: Variation of MNDO total energies with dihedral angle in hydrogen peroxide.

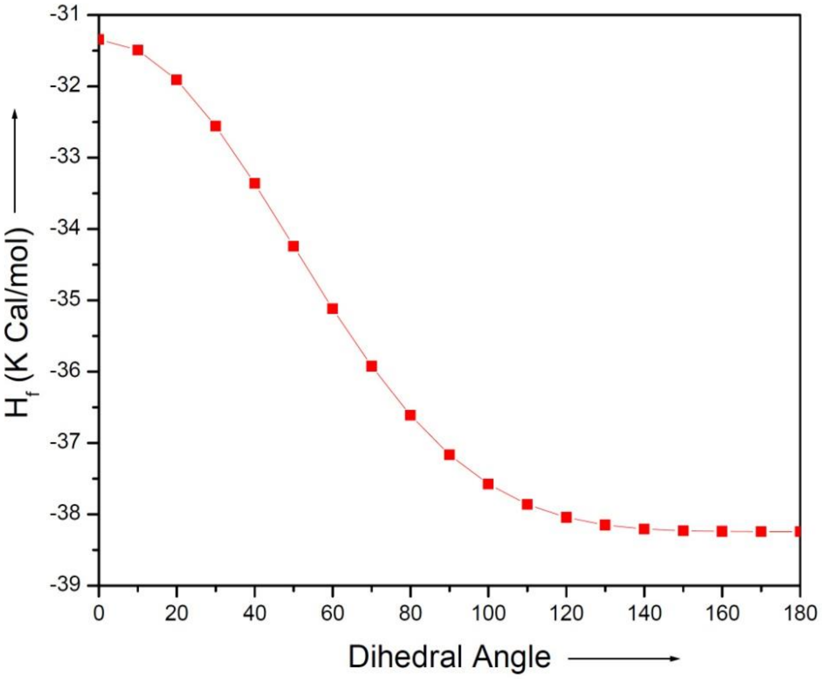

Fig. 3: Variation of MNDO heat of formation with dihedral angle in hydrogen peroxide.

The ab-initio calculations were performed using several basis set and in each case the geometry optimized starting from *cis*, *trans* and *gauche* confirmations while with starting geometries of *cis* or *trans* type the symmetry was not disturbed by the optimization processor the stable structure was found invariable to be of the “Open Book” form. The results obtained are summarized in Table-2. The O-O bond length is consistently under estimated in all cases, MNDO being the worst. The 4-31G basis set were used, uses four Gaussian in one contraction for 1s and two contractions involving 3 and 1 Gaussian respectively for the valence (2s and 2p) orbitals. In the 4-31* basis polarization functions are added (d for oxygen and p for hydrogen). The Huzinaga Dunning basis is of double zeta quality it is seen that polarization functions improve the dihedral angle.

In table-3 shows the barriers calculated by the various methods. Again we have seen that the inclusion of polarization function drastically improves the *trans* barrier, the best result being obtained with the Huzinaga Dunning basis with polarization.

The importance of geometry optimization in the calculation of barrier cannot be over emphasized. There performed a series of calculation at the STO-3G level using fixed bond length and angle but varying the dihedral angle the other parameters being given values corresponding to the stable configuration found using STO-3G basis. For comparison a similar calculation was made using the double zeta plus polarization basis and the result are shown in Fig. 4. The superior quality of the basis set has rescued the barrier in this case but its magnitude is much smaller then when optimization is performed for the various forms separately.

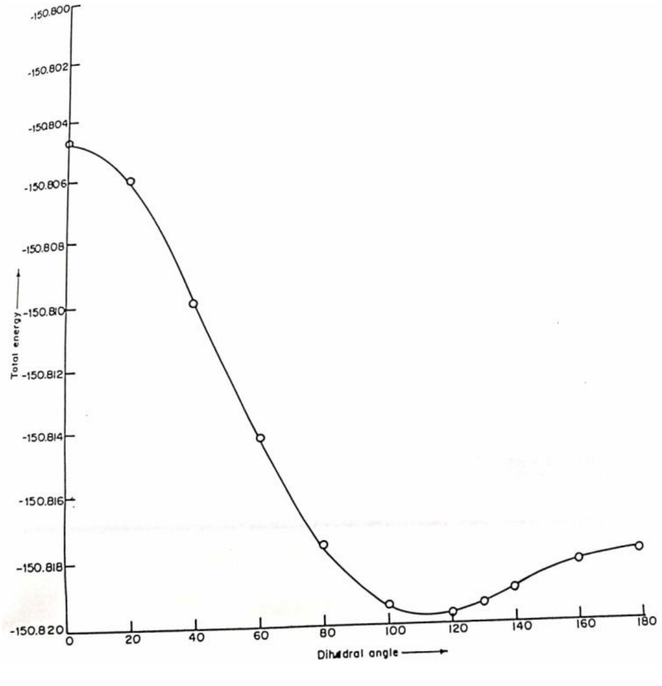

Fig. 4: Variation of Double zeta plus polarization basis total energy with dihedral angle in hydrogen peroxide.

The results of our calculations on hydrazine are summarized in Table-4. Both MNDO and STO-3G predicted the *trans* geometry to be stable whereas, in the 4-31G basis equilibrium geometry occurs at a inter group angle of 129.8°. The barriers obtained are 5.71 and 14.15 kcal/mol in this case we could not complete the 4-31G* calculation, as the calculation took ordinate amount of time for optimization. The results obtained for ethane are summarized in Table-5. The MNDO result for the barrier is too low whereas the STO-3G result is quite good. Since the minimal basis result was reasonable other basis sets were not tried in this case.

Table-1: Total geometry optimization by MNDO method for hydrogen peroxide.

Starting Configuration (Dihedral Angle)	**Optimized geometry results**		
	Total energy (eV)	**Heat of formation (kcal)**	**Dihedral angle (Degree)**
Trans	-670.89184	-38.24221	180.1
Cis	-670.59268	-31.34339	0.5
140°	-670.89084	-38.21921	143.8
150°	-670.89115	38.22639	147.0

Table-2: Equilibrium geometry of H_2O_2 by various methods.

Parameters / **Methods**	**r_{O-H} (Å)**	**r_{O-O} (Å)**	**Angle O-O-H (Degree)**	**Dihedral angle (Degree)**
MNDO	0.9607	1.2963	107.074	180.0
STO-3G	1.0034	1.3947	101.14	119.2
4-31G	0.9556	1.4659	101.34	145.2
4-31G*	0.9450	1.3972	102.24	119.9
Huzinaga Dunning	0.9563	1.4399	103.01	130.8
Huzinaga Dunning + Polarization	0.9477	1.3932	102.31	119.1
Exp.	0.9500	1.4750	94.8	119.8 111.5

Table-3: Barriers in hydrogen peroxide (H_2O_2).

Basis	***Cis***		***Trans***	
	Hartree	**kcal/mol**	**Hartree**	**kcal/mol**
STO-3G	0.0176	10.992	0.000196	0.1226
4-31G	0.01814	11.386	0.000164	0.103
4-31G*	0.013676	8.514	0.001325	0.825
Huzinaga Dunning	0.01657	10.324	0.000012	0.0075
Huzinaga Dunning +Polarzation	0.01299	8.088	0.00169	1.053
MNDO	0.111	6.898	---	---
Exp.		7.327±0.17	---	1.107±0.05

Table-4: Barriers and equilibrium geometry of hydrazine (NH_2NH_2).

Method	**r_{N-N} ((Å)**	**r_{N-H} (Å)**	**Angle N-N-H (Degree)**	**Angle N-N-H (Degree)**	**Barriers**		**Dihedral angle (Degree)**
					Hartree	**kcal**	
MNDO	1.3974	1.0209	107.2	110.1	0.0127	7.96	180
STO-3G	1.4818	1.0414	103.4	103.4	0.0167	10.41	180
4-31G	1.3989	0.9912	113.13 107.47	115.5	0.0091 0.0227	5.71 14.15	129.8
Exp.	1.449	1.022	112.0	106.0	---	3.141	90

Table-5: Geometry and barrier to rotation in ethane (C_2H_6).

Method	**r_{C-H} (Å)**	**r_{C-C} (Å)**	**Angle C-C-H (Degree)**	**Barrier**	
				Hartree	**kcal**
MNDO	1.1092	1.5208	111.2	0.0016	1.0139
STO-3G	1.0873	1.5403	108.1	0.0046	2.854
Exp.	1.091	1.536	110.9	--	2.98

IV. CONCLUSION

The barrier to internal rotation in hydrogen peroxide (H_2O_2), hydrazine (NH_2NH_2) and ethane (C_2H_6) are calculated using ab-initio and semi-empirical MNDO methods and the results are compared with experimental data. The MNDO barriers are seen to be too low and in the case of hydrogen peroxide and hydrazine, only one barrier is obtained. The ab-initio values using minimal basis STO-3G calculations are satisfactory for ethane, but in hydrogen peroxide and hydrazine reasonable results are obtained only on using split valence or double-zeta basis including polarization functions. The MNDO and STO-3G as per the obtained data predicted the *trans* geometry to be stable, while in the 4-31G basis equilibrium geometry occurs at a inter group angle of 129.8°. The barriers obtained are 5.71 and 14.15 kcal/mol.

V. ACKNOWLEDGMENT

Authors are thankful to the Dr. P. P. Thankachan, Department of Chemistry, I.I.T. Roorkee, Roorkee for their invaluable guidance, constructive criticism, thought provoking discussions and painstaking efforts throughout the work.

REFERENCES

[1] M. Born and J. R. Oppenheimer; Quantum Theory of the Molecules," *Annalen der Physik*, Vol. 84, 1927, pp. 457-484. doi:10.1002/andp.19273892002

[2] M. D. Newton, W. A. Lathan, W. J. Hehre, J. A. Pople; Self-Consistent Molecular Orbital Methods. V. *Ab Initio* Calculation of Equilibrium Geometries and Quadratic Force Constants. *J. Chem. Phys*., 52, 4064 (1970).

[3] T. A. Albright, J. K. Burdett, Myung-Hwan Whangbo; Orbital Interactions in Chemistry, 2nd Edition, Wiley (2013).

[4] C. C. J. Roothaan; Self-Consistent Field Theory for Open Shells of Electronic Systems *Rev. Mod. Phys*., 32, 179 (1960).

[5] C. C. J. Roothaan; New Developments in Molecular Orbital Theory. *Rev. Mod. Phys*., 23, 69 (1951).

[6] M. J. S. Dewar and W. Thiel; Ground states of molecules. 38. The MNDO method. Approximations and parameters; *J. Am. Chem. Soc*., 99, 4899 (1977).

[7] T. H. Dunning, N. W. Winter; Theoretical determination of the barriers to internal rotation in hydrogen peroxide; *J. Chem. Phys*., 63, 1847 (1975); https://doi.org/10.1063/1.431561.

[8] L. Song, M. Liu, W. Wu, Q. Zhang, Y. Mo; Origins of Rotational Barriers in Hydrogen Peroxide and Hydrazine *J. Chem. Theory Comput*., 1, 395 (2005).

[9] R. M. Pitzer and W. N. Lipscomb; Calculation of the Barrier to Internal Rotation in Ethane. *J. Chem. Phys*., 39, 1995 (1963).

[10] D. A. Dows; Infrared Spectrum of Crystalline Boron Trifluoride; *J. Chem. Phys*., 31, 1637 (1959).

[11] E. Clementi, D. R. Davis; Barrier to Internal Rotation in Ethane; *J. Chem. Phys*., 45, 2593 (1966).

[12] L. Pedersen, K. Morokuma; Ab Initio Calculations of the Barriers to Internal Rotation of CH_3CH_3, CH_3NH_2, CH_3OH, N_2H_4, H_2O_2, and NH_2OH; *J. Chem. Phys*., 46, 3941 (1967).

[13] R. M. Stewens; Accurate SCF Calculation for Ammonia and Its Inversion Motion, *J. Chem. Phys*. 55, 1725 (1971).

[14] S. Weiss and G. E. Leroi; Direct Observation of the Infrared Torsional Spectrum of C_2H_6, CH_3CD_3, and C_2D_6, *J. Chem. Phys*., 48, 962 (1968).

[15] U. Kaldor and I. Shavitt; LCAO–SCF Computations for Hydrogen Peroxide, J. Chem. Phys. 44, 1823 (1963).

[16] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, Internal rotation in hydrogen peroxide: the far-infrared spectrum and the determination of the hindering potential (T/E), *J. Chem. Phys*., 42, 1931 (1965).

[17] W. H. Fink, L. C. Allen; Origin of Rotational Barriers. II. Methylamine and Improved Wavefunctions for Hydrogen Peroxide, *J. Chem. Phys*., 46, 2276 (1967).

[18] T. H. Dunning, Jr. R. C. Winter; Hartree- Fock calculation of the Barriers to Internal Rotation of hydrogen peroxide; *Chem. Phys. Lett*., 11, 194 (1971).

[19] T. Kasuya, T. Kojima; Internal motions of hydrazine; *J. Phys. Soc. Japn*., 18, 364 (1963).

[20] W. Thiel; Semiempirical NDDO calculations with STO-3G and 4-31G basis sets. *Theoretica chimica acta*, 59, 191 (1981).

[21] J. F. Gaw, N. C. Handy, P. Palmieri, and A. Degli Esposti, The anharmonic potential function of methylene fluoride. SCF *ab initio* computations of the cubic force field and analysis of vibration–rotation interaction constants, *J. Chem. Phys*., 89, 959 (1988).