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$_2$O$_2$), hydrazine (NH$_2$NH$_2$) and ethane (C$_2$H$_6$) 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$_2$O$_2$), hydrazine (NH$_2$NH$_2$) and ethane (C$_2$H$_6$), 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 $Z_\alpha$ (where $\alpha$ varies from 1 to $v'$) and $n'$ electrons, Hamiltonian equation be able to written (in atomic units) like,

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

(1)

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

Where the mass of nucleus is $M_\alpha$ and unit of $m_e$ is $\alpha$. 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

$$ \psi = \psi_e \psi_e $$

(2)

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

$$ H_e \psi_e = E_e \psi_e $$

(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 $\psi_e$ as a function of nuclear co-ordinates and the nuclear motion is then described by the equation.

$$ (T_n + E_e) \psi_n = E_n \psi_n $$

(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.

$$\psi(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} v_1(1)v_1(2)v_1(3)\ldots\ldots v_1(N) \\ v_2(1)v_2(2)v_2(3)\ldots\ldots v_2(N) \\ \vdots \ \vdots \\ v_n(1)v_n(2)v_n(3)\ldots\ldots v_n(N) \end{vmatrix}$$

(5)

Here the $v_{\alpha\beta}$ 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.

$$<H> = \frac{<\psi | H | \psi>}{<\psi | \psi>}$$

(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 $\alpha$ and $\beta$ 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
$\psi(1, 2, ..., N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \phi_1(3) & \cdots & \phi_1(N) \\ \phi_1(1) & \phi_1(2) & \phi_1(3) & \cdots & \phi_1(N) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_{N/2}(1) & \phi_{N/2}(2) & \phi_{N/2}(3) & \cdots & \phi_{N/2}(N) \\ \phi_{N/2}(1) & \phi_{N/2}(2) & \phi_{N/2}(3) & \cdots & \phi_{N/2}(N) \end{vmatrix}$ (7)

Where the pair of orbitals $\Phi_i$ and $\phi_i$ have the same space part and have $\alpha$ and $\beta$ spin respectively.

Molecular orbitals are usually constructed as linear combinations of atomic orbitals (LCAO). However, it is current computational practice to seek them as a linear 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

$$u_{iA} = (\text{spherical harmonic}) \times r_A^{n-1} e^{-\alpha r_A}$$ (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 3$p$’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 $\xi$ 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.

$$X = x^1(1) x^2(2) x^3(3) e^{-\alpha x^2}$$ (9)

However, they have the wrong cusp behavior, as the Slater type 1$s$ 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 linear 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 linear combination of basis function $\Phi_i$; and the ground state of the system is written as a single Slater determinant (Equation 7).

$$u_i = \sum_{p=1}^{m} C_{ip} \Phi_p$$ (10)

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

$$\tilde{H} = \sum_{i=1}^{N} H_i + \sum_{i<j}^{N} \frac{1}{t_{ij}}$$ (11)

Where $\tilde{H}_i$ is the one electron operator.
\[ \hat{H}_i = -\frac{1}{2} \nabla^2_i - \sum_{a=1}^{\alpha} \frac{Z_a}{R_{ia}} \]  

The total system energy has been shown to be

\[ E = 2 \sum_{i=1}^{N/2} \hat{H}_i + \sum_{i=1}^{N/2} \sum_{j \neq i}^{N/2} (2J_{ij} - K_{ij}) \]  

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

\[ H_i = \langle \mathbf{u}_i(1) | \hat{H} | \psi_i(1) \rangle \]  

\[ J_{ij} = \langle \mathbf{u}_i(1) \mathbf{u}_j(2) | \frac{1}{\rho_{ij}} | \mathbf{u}_i(1) \mathbf{u}_j(2) \rangle \]  

\[ K_{ij} = \langle \mathbf{u}_i(1) \mathbf{u}_j(2) | \frac{1}{\rho_{ij}} | \mathbf{u}_i(2) \mathbf{u}_j(1) \rangle \]

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

\[ F_{ui} = \mathcal{E}_i \mathbf{u}_i \]  

where the operator \( F \) is defined by

\[ F = \hat{H} + \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) \]

Where \( J_{ij}, K_{ij} \) are defined through

\[ \langle \mathbf{u}_i | J_{ij} | \mathbf{u}_i \rangle = J_{ij} \]  

\[ \langle \mathbf{u}_i | K_{ij} | \mathbf{u}_i \rangle = K_{ij} \]

The orbital energies are given by

\[ \mathcal{E}_i = H_i + \sum_{j=1}^{N/2} (2J_{ij} - K_{ij}) \]  

\[ E = \sum_{i=1}^{n}(H_i + \mathcal{E}_i) \]

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 methods only the valance electrons are explicitly treated. The valance shells molecular orbitals (\( \psi_v \)) are correspond to by liner combination of minimum basis of valence shell atomic orbitals (\( \phi_v \));

\[ \psi_v = \sum_{v} C_{vi} \phi_v \]  

The coefficient \( C_{vi} \) is established from Roothaan-Hall equation, which were assumed in the form of NDDO approximation such as,
where, eigen value of the MO ψᵢ is Eᵢ and δᵢν the kronecher δ. The elements $F_{µν}$ of the Fock matrix are the sum of a one electron part $H_{µν}$, a two electron part and the electronic energy $E_{el}$ is given by

$$H = \frac{1}{2} \sum_µ \sum_ν P_{µν} (H_{µν} + F_{µν})$$

Where $P_{µν}$ is an element of the bond order matrix. It is assumed that the AO’s $ϕ_A$ and $ϕ_B$ at atom B (A ≠ B). In this notation the NDDO Fock matrix elements are

$$F_{µµ} = U_{µµ} + \sum_B V_{µµ} B + \frac{1}{2} (\mu\mu, νν) + \sum_B \sum_{λ, σ} P_{λσ} (\mu\mu, λσ)$$

$$F_{µν} = \sum_B V_{µν} B + \frac{1}{2} P_{µν} [3(\mu\mu, νν) - (\mu\mu, νν)] + \sum_B \sum_{λ, σ} P_{λσ} (\mu\mu, λσ)$$

$$F_{µλ} = B_{µλ} - \frac{1}{2} \sum_μ \sum_ν P_ν (µµ, λσ)$$

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

$$E_{mol}^{tot} = E_{el} + \sum_A E_{core}^{AB}$$

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.

$$H_f^{mol} = E_{el}^A + \sum_A ΔH_f^A$$

The electronic energies of the atom are calculated from restricted single-determinant 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 MINDO 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 [4s3p4d/2s1p] 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 date 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 stabiles. 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 H2O2 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 NH2 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 (H2O2), hydrazine (NH2NH2) and ethane (CH3CH3) 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 invariably 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 important 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 an 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 tookordinate 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.

<table>
<thead>
<tr>
<th>Starting Configuration (Dihedral Angle)</th>
<th>Optimized geometry results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total energy (eV)</td>
</tr>
<tr>
<td><strong>Trans</strong></td>
<td>-670.89184</td>
</tr>
<tr>
<td><strong>Cis</strong></td>
<td>-670.59268</td>
</tr>
<tr>
<td>140°</td>
<td>-670.89084</td>
</tr>
<tr>
<td>150°</td>
<td>-670.89115</td>
</tr>
</tbody>
</table>

**Table-2:** Equilibrium geometry of H$_2$O$_2$ by various methods.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>r$_{O-H}$ (Å)</th>
<th>r$_{O-O}$ (Å)</th>
<th>Angle O-O-H (Degree)</th>
<th>Dihedral angle (Degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Methods</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MNDO</td>
<td>0.9607</td>
<td>1.2963</td>
<td>107.074</td>
<td>180.0</td>
</tr>
<tr>
<td>STO-3G</td>
<td>1.0034</td>
<td>1.3947</td>
<td>101.14</td>
<td>119.2</td>
</tr>
<tr>
<td>4-31G</td>
<td>0.9556</td>
<td>1.4659</td>
<td>101.34</td>
<td>145.2</td>
</tr>
<tr>
<td>4-31G*</td>
<td>0.9450</td>
<td>1.3972</td>
<td>102.24</td>
<td>119.9</td>
</tr>
<tr>
<td>Huzinaga Dunning</td>
<td>0.9563</td>
<td>1.4399</td>
<td>103.01</td>
<td>130.8</td>
</tr>
<tr>
<td>Huzinaga Dunning + Polarization</td>
<td>0.9477</td>
<td>1.3932</td>
<td>102.31</td>
<td>119.1</td>
</tr>
<tr>
<td>Exp.</td>
<td>0.9500</td>
<td>1.4750</td>
<td>94.8</td>
<td>119.8</td>
</tr>
</tbody>
</table>
Table 3: Barriers in hydrogen peroxide (H₂O₂).

<table>
<thead>
<tr>
<th>Basis</th>
<th>Cis</th>
<th>Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hartree</td>
<td>kcal/mol</td>
</tr>
<tr>
<td>STO-3G</td>
<td>0.0176</td>
<td>10.992</td>
</tr>
<tr>
<td>4-31G</td>
<td>0.01814</td>
<td>11.386</td>
</tr>
<tr>
<td>4-31G*</td>
<td>0.013676</td>
<td>8.514</td>
</tr>
<tr>
<td>Huzinaga Dunning</td>
<td>0.01657</td>
<td>10.324</td>
</tr>
<tr>
<td>Huzinaga Dunning + Polarzation</td>
<td>0.01299</td>
<td>8.088</td>
</tr>
<tr>
<td>MNDO</td>
<td>0.111</td>
<td>6.898</td>
</tr>
<tr>
<td>Exp.</td>
<td>7.327±0.17</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 4: Barriers and equilibrium geometry of hydrazine (NH₂NH₂).

<table>
<thead>
<tr>
<th>Method</th>
<th>rN-N (Å)</th>
<th>rN-H (Å)</th>
<th>Angle N-N-H (Degree)</th>
<th>Angle N-N-H (Degree)</th>
<th>Barriers</th>
<th>Dihedral angle (Degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hartree</td>
<td>kcal</td>
</tr>
<tr>
<td>MNDO</td>
<td>1.3974</td>
<td>1.0209</td>
<td>107.2</td>
<td>110.1</td>
<td>0.0127</td>
<td>7.96</td>
</tr>
<tr>
<td>STO-3G</td>
<td>1.4818</td>
<td>1.0414</td>
<td>103.4</td>
<td>103.4</td>
<td>0.0167</td>
<td>10.41</td>
</tr>
<tr>
<td>4-31G</td>
<td>1.3989</td>
<td>0.9912</td>
<td>113.13</td>
<td>107.47</td>
<td>0.0091</td>
<td>5.71</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.449</td>
<td>1.022</td>
<td>112.0</td>
<td>106.0</td>
<td>---</td>
<td>3.141</td>
</tr>
</tbody>
</table>

Table 5: Geometry and barrier to rotation in ethane (C₂H₆).

<table>
<thead>
<tr>
<th>Method</th>
<th>rC-H (Å)</th>
<th>rC-C (Å)</th>
<th>Angle C-C-H (Degree)</th>
<th>Barrier</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Hartree</td>
</tr>
<tr>
<td>MNDO</td>
<td>1.1092</td>
<td>1.5208</td>
<td>111.2</td>
<td>0.0016</td>
</tr>
<tr>
<td>STO-3G</td>
<td>1.0873</td>
<td>1.5403</td>
<td>108.1</td>
<td>0.0046</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.091</td>
<td>1.536</td>
<td>110.9</td>
<td>--</td>
</tr>
</tbody>
</table>
IV. CONCLUSION

The barrier to internal rotation in hydrogen peroxide (H₂O₂), hydrazine (NH₂NH₂) and ethane (C₂H₆) 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 an inter group angle of 129.8°. The barriers obtained are 5.71 and 14.15 kcal/mol.

V. ACKNOWLEDGMENT

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