ABSTRACT. The origin of barriers to internal rotation of hydrogen peroxide and ethane is investigated by using the concept of Bonding and Antibonding Regions. The strong bond formations between the axial and end atoms on the same side make the real charge densities in these molecules less dependent on conformations than those in the hypothetical molecules having no axial atoms. Thus, the existence of the axial atoms should induce the migration of the transition density from the Bonding region to the Antibonding region. Barrier to internal rotation can be understood in terms of this migration of the transition density to such an extent that the change in nuclear–nuclear repulsion energy becomes the dominating part of the total perturbation energy.

1. INTRODUCTION

Barrier to internal rotation has been one of the most interesting subjects to chemists, ever since it was found in 1936.1 It is very important to understand the nature of the barrier, which is related to the conformational and biological activity of large molecule. The barrier heights have been successfully evaluated for small molecules by SCF scheme2–5 or perturbation theory.6

Early in 1960’s, Clinton,7a Karplus and Parr,7b and Ruedenberg7c showed that the difference of the nuclear repulsion energy yields a barrier of the correct sign and magnitude. Thereafter, in the effort to search the barrier ori-
gin, the total perturbation energy accompanying the conformational change has been partitioned into various components and the major contributing component to barrier has been sought.\textsuperscript{5,6,10} Wyatt and Parr\textsuperscript{6} suggested, through the use of the Integral Hellmann-Feynman Theorem (IHF),\textsuperscript{9} that the change of the electronic energy of ethane comes mainly from the three-fold transition density component in the vicinity of protons. Fink and Allen\textsuperscript{6} attempted to analyze the barrier mechanism by the partition of the total energy into one- and two-electron components. Allen\textsuperscript{10} classified the barriers as the attractive and repulsive dominant, and discussed the nature of the barriers of ethane and aldehyde by using the electron-density-distribution plots.\textsuperscript{31}

Another approach to the barrier origin is based on the localized bond orbital descriptions.\textsuperscript{12,13} In 1968, Sovers \textit{et al.}\textsuperscript{12} pointed out from the simple bond-function analysis that the orbital orthogonality, which is introduced by the Pauli Exclusion Principle, is the prime factor in the rotational barrier of ethane. They extended the similar analysis to methanol in 1974.\textsuperscript{126} These results have been reconfirmed by many other workers.\textsuperscript{13}

In this paper, we attempt to give a new and simple interpretation of the barrier origin by partitioning the total perturbation energy \((\Delta E)\) into the change of the nuclear-nuclear repulsion energy \((\Delta E_{nn})\) and that of the electronic energy \((\Delta E_{el})\) using IHF. It may be easily shown from the experimental results of barriers that \(\Delta E_{nn}\) in general, has an opposite phase to \(\Delta E_{el}\), which is less than \(\Delta E_{nn}\) in absolute value. Namely, \(\Delta E_{el}\) attenuates \(\Delta E_{nn}\) as pointed out by Karplus \textit{et al.}\textsuperscript{1} Thus the origin of the internal rotation barrier might be comprehended not by seeking the major component of \(\Delta E_{el}\) (or \(\Delta E\)), but by answering the most fundamental question: "Why is the magnitude of \(\Delta E_{el}\) less than that of \(\Delta E_{nn}\)?" To do so, we introduce the new concept of the Bonding and Antibonding Regions,\textsuperscript{10} and compare the transition density\textsuperscript{15} of the actual molecule with that of the hypothetical molecule which has the same nuclear framework except the axial atoms and has the same perturbation operators, \(\Delta V\) and \(\Delta V_{av}\).

The concept of the Bonding and Antibonding Regions is briefly outlined in Section 2. In Sec. 3, the barrier origin of \(\text{H}_2\text{O}_2\) which has a relatively large barrier and has a realistic reference molecule, \(\text{H}_2\), is analyzed by using this concept. The barrier of ethane is discussed from the same viewpoint.

## 2. Bonding and Antibonding Regions

Only a short outline of the Bonding and Antibonding Regions will be given here since full details can be found in Paper I.\textsuperscript{14} We will use the same notations as in Paper I without any further comments.

According to IHF, the perturbation energy due to the change of the nuclear framework from \(R_o\) to \(R\) is given by

\[
\Delta E(R_o \rightarrow R) = \int \Delta \rho(1) \rho_{R_o}(1) \, d\tau + \int \Delta E_{nn}(R_o \rightarrow R) \, d\tau \\
\equiv \Delta E_{el}(R_o \rightarrow R) + \Delta E_{nn}(R_o \rightarrow R) \tag{1}
\]

Transition density, \(\rho_{R_o}(1)\), is positive definite and can be approximated to the average real charge density, \(\frac{1}{2}(\rho_{R_o}(1) + \rho_{R}(1))\). This approximation seems to be a good one in all space except the vicinity of nuclear sites. Thus, one can guess the general pictures of the real charge densities from the fictitious transition density.

From the positive-definiteness of the transition density, one can divide the transition density space into the Bonding and Antibonding
Regions solely by the sign of \( \Delta \nu(1) \):

\[
\Delta E_{\text{el}}(R_0 \rightarrow R) = \int \Delta \nu(1) \rho_{R \rightarrow R}(1) \, d\tau_1 \quad \text{(negative)}
\]

\[
+ \int \Delta \nu(1) \rho_{R \rightarrow R}(1) \, d\tau_1 \quad \text{(positive)}
\]

The boundary surfaces of these two regions are given by the solutions of \( \Delta \nu(1) = 0 \). The transition charge element \( \rho_{R \rightarrow R}(1) \, d\tau_1 \) in the Bonding Region contributes to the lowering of energy, and \( \rho_{R \rightarrow R}(1) \, d\tau_1 \) in the Antibonding Region acts in the opposite way during the change of the nuclear framework from \( R_0 \) to \( R \).

3. RESULTS AND DISCUSSIONS

The hydrogen peroxide molecule, \( \text{H}_2\text{O}_2 \), which may be the simplest molecule having the barrier to internal rotation, has moderately high symmetry so that one is able to prove the existence of the extreme values of \( E_{\text{sh}} \), \( E_{\text{an}} \), and \( E \) at both trans and cis conformations without an explicit use of the wavefunctions. However, it has fairly larger barrier\(^{18} \) in comparison with such prototype molecules listed in Table 1. Thus, under small modifications in bond lengths and wavefunctions caused by scaling,\(^{5} \) the relative phase and amplitude of \( E_{\text{sh}}(=E_{\text{g}}+E_{\text{g}}+E_{\text{ex}}) \) and \( E_{\text{an}} \) are considered to be invariant. The facts thus validate the partition of the total energy \( E \) into \( E_{\text{el}} \) and \( E_{\text{an}} \). And the partition is compatible with the use of IHF formula of Eq. (1) to be used in the following discussions. Lastly, and the most important of all, the moving part of the molecule in the process of the internal rotation has a realistic analogue. \( \text{H}_2 \) molecule, as long as the perturbation operators, \( \Delta \nu(1) \) and \( \Delta V_{\text{el}} \), are concerned.

For the purpose of analysis, trans and cis \( \text{H}_2\text{O}_2 \) are arranged to a space-fixed coordinate system\(^{4} \) as in Fig. 1. At the same time, \( \text{H}_2 \) molecules, which have exactly equivalent protonic configurations to the trans and cis \( \text{H}_2\text{O}_2 \) (and will be called hereafter as trans and cis \( \text{H}_2 \), respectively) are similarly arranged to the coordinate systems. Assuming a hypothetical situation in which the protons originally at the

![Table 1](image)

*in kcal/mole. *experimental values are taken from Ref. 13 unless otherwise stated, *calculated from the data in Ref. 19 unless otherwise stated, \( \Delta E_{\text{el}} = \Delta E_{\text{ex}} = \Delta E_{\text{an}} \). *see Ref. 5b, *see Ref. 5a, *see Ref. 18, *see Ref. 20. * see Ref. 3c.

![Fig. 1](image)

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Fig. 2. (A) Energy vs. torsional angle of H₄ obtained from the calculations of McLean et al. by constraining protons on Sections A and G. (B) Schematic energy diagram vs. torsional angle of H₂O₂ obtained from SCF calculations by Pitzer and Palke.

**Table 2. Energy changes in internal rotation.**

<table>
<thead>
<tr>
<th></th>
<th>E_{calc}</th>
<th>E_{ex}</th>
<th>E_{el}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>13.05</td>
<td>70.44</td>
<td>-57.39</td>
</tr>
<tr>
<td>H₂</td>
<td>-25.66</td>
<td>70.44</td>
<td>-97.10</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>3.28</td>
<td>4.70</td>
<td>-1.42</td>
</tr>
<tr>
<td>H₂</td>
<td>-16.78</td>
<td>4.70</td>
<td>-21.48</td>
</tr>
</tbody>
</table>

*in kcal/mole, calculated barrier height, ΔE_{el} = ΔE_{calc} - ΔE_{ex}, see Ref. 4, energy changes during the same protonic framework change of H₂O₂ are calculated from the data in Ref. 17, see Ref. 2, energy changes during the same nuclear framework change of C₂H₂ are obtained from our CNDO calculations.

Table 2 and the energy formulae:

\[ ΔE_{el}(trans\rightarrow cis) = \int Δv(1)ρ_{el}^0(1)d\gamma + ΔE_{ex}(trans\rightarrow cis) \]  

(3)

\[ ΔE_{el}(trans\rightarrow cis) = \int Δv(1)ρ_{el}^0(1)d\gamma + ΔE_{ex}(trans\rightarrow cis) \]  

(4)

where \( ΔE_{ex} \) and \( Δv(1) \) are common to H₂ and H₂O₂ and

\[ Δv(1) = \begin{bmatrix} -\frac{1}{2} \sqrt{\frac{1}{r_{H}}} \\ +\frac{1}{2} \sqrt{\frac{1}{r_{O}}} \end{bmatrix} \] (cis protons) \( \begin{bmatrix} -\frac{1}{2} \sqrt{\frac{1}{r_{H}}} \\ +\frac{1}{2} \sqrt{\frac{1}{r_{O}}} \end{bmatrix} \) (trans protons)

\( ΔE_{el}(trans\rightarrow cis) \) is always given exactly if one knows the exact protonic arrangements. Thus the total perturbation energies of H₂O₂ and H₂ can be compared solely in terms of the electronic perturbation energies, \( ΔE_{el}^{trans} \) and \( ΔE_{el}^{cis} \), which in turn may be analyzed through the transition densities, \( ρ_{el}^{trans}(1) \) and \( ρ_{el}^{cis}(1) \) having the common Bonding and Antibonding Regions. Fig. 3 shows the contour maps of \( Δv(1) \) depicted in Sections A, B, C, and D of the cylinder in Fig. 1. Because of the rather large absolute values of \( Δv(1) \) in the vicinity of the protonic sites, the transition density near the sites would be expected to play the crucial role. The transition density contour maps in each section for H₂ and H₂O₂ are shown in Figs. 4 and 5, respectively. Since the 𝑦-axis of Fig. 1 is the...
two-fold rotation axis, the maps in Sections G, F, and E are the mirror images of those in Sections A, B, and C, respectively. $\rho_{\text{cyl}}^1(1)$ is normalized to 2 and $\rho_{\text{cyl}}^\alpha(1)$ to 18, and thus the contour intervals are chosen with the different values: 0.01 a.u. for H$_2$ and 0.09 a.u. for H$_2$O$_2$. Therefore, the direct comparison of two maps is a little awkward.

Fortunately, it can be easily shown, by the expansion of $J_\nu(1)$ in terms of the spherical harmonics, that an arbitrary density with cylindrical symmetry, $\rho_{\text{cyl}}^1(1)$, does not combine with the perturbation operator, $J_\nu(1)$, that is,

$$\int J_\nu(1) \rho_{\text{cyl}}^1(1) \, d\tau_1 = 0$$  \hspace{1em} (6)

The density, $\rho_{\text{cyl}}^1(1)$, may be the whole or a part of the cylindrical component of the transition density of H$_2$O$_2$, or the density of the oxygen molecule with the equivalent nuclear positions of oxygens in H$_2$O$_2$, or the superposed density of two atomic oxygens located

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Fig. 4. Transition density of \( \text{H}_2 \), \( \rho_0^\text{trans}(1) \), in Sections A, B, C, and D. Contour interval is 0.01 a.u. \( p \)-Orbitals in the wavefunctions by McLean et al. are not included.

at the same positions as in \( \text{H}_2 \text{O}_2 \). If the effective transition density is defined as

\[
\rho_0^\text{eff}(1) \equiv \rho_0^\text{trans}(1) - \rho_0(1) \tag{7}
\]

one may write

\[
\Delta E_{\text{H}_2\text{O}_2} (\text{trans} \rightarrow \text{cis}) = \int d\tau_1 \rho_0^\text{eff}(1) + \Delta E_{\text{ex}} (\text{trans} \rightarrow \text{cis}) \tag{8}
\]

in place of Eq. (4). Subtracting Eq. (3) from Eq. (8), the difference of the perturbation energies of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2 \) accompanying the change from \text{trans} to \text{cis} is given by

\[
\Delta E_{\text{H}_2\text{O}_2} - \Delta E_{\text{H}_2} = \int d\tau_1 \left( \rho_0^\text{trans}(1) - \rho_0(1) \right) d\tau_1 \equiv \int d\tau_1 \Delta \rho(1) d\tau_1 \tag{9}
\]

where \( \Delta \rho(1) \) is the difference between that effective transition density of \( \text{H}_2\text{O}_2 \) and the transition density of \( \text{H}_2 \), and will be called hereafter as the difference transition density. Because of the closeness of the normalizations of \( \rho_0^\text{trans}(1) \) and \( \rho_0(1) \), \( \Delta \rho(1) \) may be visualized well on
plotting. In the present work, $\rho_{0\xi}(1)$ is obtained from the square and cross terms of $1s$, $2s$, and $2p_x$ and from $2p_x^2 + 2p_y^2$ of oxygen atoms. It is normalized to circa 12. $\Delta \rho(1)$ is depicted in Fig. 6 and one observes the following from Figs. 4, 5 and 6:

(1) The transition density of $H_2$, $\rho_{1\sigma}(1)$, is more heavily distributed in the Bonding Region than in the Antibonding Region. (See Fig. 4) The fact is thus clearly consistent with the large negative value of $\Delta E_c$, $-97.10$ kcal/mole and with the observations in Paper I.

(2) Mostly positive contours of $\Delta \rho(1)$ in the central zones of each section (see Fig. 6) imply that $\rho_{1\sigma}(1)$ contracts toward the center of each section due to the strong O-H bonds. The strong O-H bond formations make the real charge density of $H_2O_2$ less dependent on conformations than that of $H_2$. Namely, the real charge densities of $trans$ and $cis$ $H_2O_2$ do not differ greatly from each other. The conjecture is also justified from the symmetrical shape (with respect to the boundary lines) of $\rho_{1\sigma}(1)$ in Fig. 5. In other words, $\rho_{1\sigma}(1)$, and therefore $\rho_{1\sigma}(1)$,
is less bonding than $\rho_b(1)$. Consequently, the difference transition density in the Antibonding Region is distinctly dominant over that in the Bonding Region as one can see in Fig. 6. $\Delta E_e (\text{trans} \rightarrow \text{cis})$ is, however, still negative, since in the neighborhood of the protonic sites in the Bonding Region is slightly more excessive than that in the Antibonding Region, especially in sections A, B, and C.

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From these observations, it may be concluded that a sharp rise of the electronic energy of $\text{H}_2\text{O}_2$ relative to $\text{H}_2$ during the change from trans to cis (39.71 kcal/mole, see Table 2), to such an extent that $|\Delta E_e| < |\Delta E_a|$ in $\text{H}_2\text{O}_2$, can be understood in terms of the migration of the transition density from the Bonding Region to the Antibonding Region due to the strong bond formations between oxygen and hydrogen.
on the same side.

It is, however, impossible to pinpoint the part of molecule which offers the major contribution to $\Delta E^\text{dihed} - \Delta E^\text{ax}$, since it depends on both $\Delta r(1)$ and $\Delta \rho(1)$. Furthermore, "the origin of the barrier to internal rotation" may be interpreted as the major and substantial cause of barrier formation at a certain dihedral angle, and in the case of $\text{H}_2\text{O}_2$, it is not $\Delta E^\text{ax}$ but $\Delta E^\text{nn}$ which forms the barrier at the cis position. Introduction of an improved wavefunction may alter the numerical value of the barrier and may show both cis and trans barriers through the delicate balance of $E^\text{ax}$ and $E^\text{nn}$, but it would not change the qualitative picture of the transition density presented in this work.

In order to analyze the barrier of ethane, C$_2$H$_6$, from the similar viewpoint, the CNDO calculations on the hypothetical eclipsed and staggered H$_2$ molecules have been performed and the results are listed in Table 2. The electronic perturbation energy in ethane accompanying the change from staggered to eclipsed is smaller in magnitude than that in H$_2$, just as in the case of H$_2$O$_2$ vs. H$_2$. However, it fails to visualize the migration of the transition density to the Antibonding Region, because the very small difference of the perturbation energies of ethane and H$_2$, about 20 kcal/mole, and, in addition, the existence of six boundary surfaces make the contour lines of the transition density prohibitively delicate for visualization.

The transition densities both in the Bonding Region and in the Antibonding Region have the same symmetry properties as the perturbation operator, $\Delta r(1)$, and thus it would be rather inadequate to say simply that the origin of barrier is in a certain symmetry component of the transition density.

4. CONCLUDING REMARKS

The origin of the barriers to internal rotation of hydrogen peroxide and ethane is analyzed in terms of the transition density. Adopting the hydrogen molecules which are strategically arranged in the space as reference, it is shown that the migration of the transition density to the Antibonding Region, due to the existence of the axial atoms, causes the decrease of the magnitude of the electronic perturbation energy to such an extent that the change of the nuclear-nuclear repulsion energy becomes the dominant portion of the total perturbation energy. The increase of the transition density in the Antibonding Region has its origin in the bond formations between the axial and end atoms on the same side. Thus the real charge densities of the molecules with axial atoms are less dependent on conformations than those of the hypothetical molecule having no axial atoms.

If each integral of Eq. (2) can be evaluated separately in any given part of molecule, for example, in each section with a finite thickness in Fig. 1, the concept of the Bonding and Antibonding Regions may be more useful even in the quantitative analysis of such problems involving the small electronic energy change as the rotation barrier of ethane.

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16. $d\omega(1)$ and $dV\omega$ are the perturbation operators of nuclear-electron attraction and nuclear-nuclear repulsion, respectively.