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Barriers to the Internal Rotation and Observables of the Ground State for Hydrogen Peroxyde

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SCF energy and one electron properties of the H_2O_2 molecule have been calculated by using a basis of 52 STO's. The minimum total energy reached is -150.83188 a.u. By carrying out the calculation for three different geometrical configurations a reasonable agreement with experimental values of the barriers to the internal rotation is obtained.

Die SCF-Energie und die Einelektroneneigenschaften des H_2O_2-Moleküls werden mit einer Basis von 52 Slaterorbitalen berechnet. Als minimale Gesamtenergie werden der Wert von $-150{,}83188$ a.E. erreicht. Die Ergebnisse für 3 verschiedene Geometrien liefern eine befriedigende Übereinstimmung mit dem experimentellen Wert der Barriere für die innere Rotation.

L'énergie SCF et les propriétés monoélectroniques de la molécule H_2O_2 ont été calculées en utilisant une base de 52 orbitales de Slater. L'énergie minimum totale atteinte est -150.83188 u.a. Un accord raisonnable avec les valeurs expérimentales des barrières de rotation est obtenu en effectuant les calculs pour trois configurations géométriques différentes.

1. Introduction

In the recent years, it has become possible to achieve accurate "*ab initio*" calculations, at least for the simpler cases of polyatomic molecules, and the problem of the evaluation of the barriers to the internal rotation has drawn increased attention. Among the cases that have been considered, the H_2O_2 molecule presents a particular interest for two reasons. On the one hand, it is probably the most simple stable system (lowest number of electrons and nuclei) which shows such a type of barriers, and on the other hand, the smallness of the lower of the two barriers (1.10 kcal/mole) renders a prediction of this observable a very critical test for the calculation methods that one may utilize.

The Hartree-Fock (H.F.) scheme is still the most largely used one for *ab initio* calculations of the ground state of molecular systems, and the question as to whether this approximation is able to yield correct predictions for the barriers to the internal rotation, is still open. Many recent works [1–4] seem to give a positive answer to this question, at least in most cases. The trans barrier of the H_2O_2 molecule has, however, furnished contrasting results [1, 4, 5]. In any case one must face two difficulties. Firstly it is not easy to guess a plausible limit for the H.F. energy of a molecule in a given geometry, and sometimes the execution of calculations on more and more extended basis sets has entailed the lowering of the presumed H.F. limit. The previsions that one may guess for this limit frequently

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present errors that are at least of the same order of magnitude as the barriers that one wishes to calculate, so that it is difficult to decide whether the result obtained as a difference between two SCF energies of two different molecular geometries, represents effectively the result of the H.F. approximation. One must rather acknowledge that the majority of the calculations carried out even now, still utilizes too limited basis sets. It is evident that the only rigorous way to overcome the obstacle (and that has indeed been followed in the case of atoms and of the simplest molecules), i.e. the increasing and improvement of the basis up the attainement of the stability in the energy to the required limits, is, at present, too expensive for molecules that present barriers to the internal rotation.

In the second place, one must take into account the effect of the nuclear relaxation, i.e. the variation of the molecular geometry (distance and bond angles) together with the rotation angle of the barrier. The verifying as to whether the H.F. approximation is able to describe this effect correctly, involves the calculation of the H.F. energy for an adequate number of geometrical configurations and this is out of the actual concrete possibilities. When one has experimental indications for the geometries at the maximum and minimum of the barriers, it seems therefore preferable to evaluate the best SCF energy for these geometries. Usually, however, the geometrical data are known for the equilibrium configuration only, in addition, the same deduction of the values for the barriers from the spectroscopic experimental data, is often based on the hypothesis of the rigidity of the molecule during the rotation (this is, for instance, the case of the most reliable data for the H_2O_2 barriers [6]). The minimization of the SCF energy with respect to the geometrical parameters, produces a relaxation effect, but it is not certain that it correctly represents the physical situation.

In any case, this type of calculations implies a further increase in the cost.

In the H_2O_2 molecule, Veillard [4], on the basis of the optimization of the geometrical parameters in an SCF calculation, has emphasized the critical role of the relaxation effect.

This paper presents a SCF calculation on H_2O_2 molecule, that is carried out by employing a STO basis set, more extended than any other considered until now, and that attains an energy correspondingly lower. The results that one obtains for the two barriers by using such a basis for evaluating the energy in the *cis*- and *trans*-configurations, are near to the experimental ones. In this calculation, the relaxation effect is not considered, and it is not necessary to invoke it to attain the relative agreement with the experiment. For the equilibrium configuration, some one electron properties are also calculated and compared with experiment where possible.

2. Results and Discussion

In Fig. 1, the geometrical parameters and the position of the axes are defined. The reported parameters are assumed constant for all the values of the rotation angle; they correspond to the most plausible value in the equilibrium configuration [6]. For the angle β the values 0°, 120° and 180° were considered. The largest considered basis set is reported in Table 1; the criteria for this particular choice are essentially empirical in their origin, and it is rather useless to try to justify

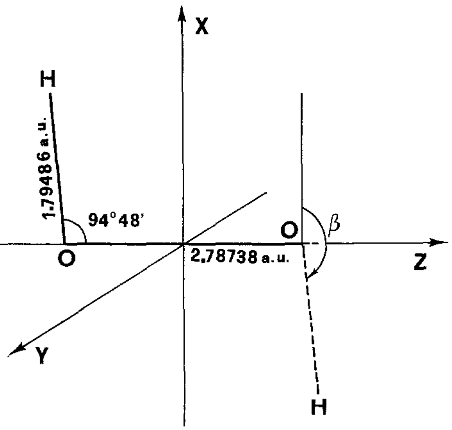

Fig. 1. Geometrical parameters

Table 1. STO's on the oxygen and hydrogen atoms

Atom	Type	Zeta
O	1*s*	12.39
	1*s*′	7.02
	2*s*	2.86
	2*s*′	1.72
	3*s*	8.65
	4*s*	1.00
	2*p*	3.76
	2*p*′	2.12
	2*p*″	1.28
	3*d*	2.00
H	1*s*	1.31
	1*s*′	2.44
	2*s*	2.30
	2*p*	2.00

Table 2. Total energy and barriers to internal rotation

	Energy (a.u.)			Barriers			
	0°	120°	180°	*cis*		*trans*	
				(a.u.)	(kcal/mole)	(a.u.)	(kcal/mole)
A[a]	−150.81459	−150.83188	−150.83073	0.01729	10.9	0.00115	0.72
B[b]	−150.81168	−150.82853	−150.82754	0.01685	10.6	0.00099	0.62
C[c]		−150.83165	−150.83043			0.00122	0.76
$(-V/2T)$[a]	1.00056	1.00069	1.00067				
Expt.[d]					7.04		1.10

[a] With the complete basis.

[b] Without the 1*s*′ functions on the hydrogen atoms.

[c] Without the 4*s* functions on the oxygen atoms.

[d] Hunt, R. H., Leacock, R. A., Peters, C. W., Hecht, K. T.: J. chem. Physics **42**, 1931 (1965).

Table 3. Different estimates of the H.F. limit for H_2O_2[a]

$2E_O{}^b+2E_H$	-151.2130	$2E_O^{\text{H.F. h}}$	-149.6295	$2E_{OH}^{\text{H.F. i}}$	-150.8425	$E_{H_2O}^{\text{tot l}}$	-76.458	$E_{H_2O_2}^{\text{tot}}$	-151.6389
$1/2\sum_i h\nu_i{}^c$	$-\ 0.0252$	$2E_H$	$-\ 1.0$	$E_{OO}^{\text{bound j}}$	$-\ 0.0776$	$-E_{H_2O}^{\text{H.F. h}}$	$+76.089$	$-2E_{H_2O}^{\text{corr.}}$	$+\ 0.640$
$H_2+O_2=H_2O_2{}^c$	$-\ 0.0495$	$E_{H_2O_2}^{\text{bound}}$	$-\ 0.4259$	$\Delta(1/2\Sigma h\nu_i)^k$	$-\ 0.0170$	$-E_O^{\text{rel}}$	$+\ 0.049$	$-2E_O^{\text{rel}}$	$+\ 0.099$
$H_2=H+H^d$	$-\ 0.1645$	$-3E^{\text{extracorr.}}$	$+\ 0.12$	$-E^{\text{extracorr.}}$	$+\ 0.04$	$E_{H_2O}^{\text{corr.}}$	$-\ 0.320$	$E^{\text{extracorr.}}$	$-\ 0.04$
$O_2=O+O^d$	$-\ 0.1867$								
$E_{H_2O_2}^{\text{tot}}$	-151.6389	$E_{H_2O_2}^{\text{H.F.}}$	-150.94	$E_{H_2O_2}^{\text{H.F.}}$	-150.90			$E_{H_2O_2}^{\text{H.F.}}$	-150.94
$-2E_O^{\text{corr. e}}$	$+\ 0.4930$								
$-2E_O^{\text{rel. f}}$	$+\ 0.098$			$E_{H_2O}^{\text{H.F.}}=-150.92\pm0.02$					
$-3E^{\text{extracorr. g}}$	$+\ 0.12$								
$E_{H_2O_2}^{\text{H.F.}}$	~ -150.93								

[a] Values used for physical constants: 1 a.u. = 27.211644 eV, 1 eV = 8065.465 cm^{-1}. From Taylor, B.N., Park, W.H., Langenberg, D.N.: Rev. mod. Physics **41**, 375 (1969).

[b] Moore, C.E.: Atomic energy levels III. Washington: The National Bureau of Standards 1958.

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[e] Obtained as $E^{\text{expt}}-(E^{\text{H.F.}}+E^{\text{rel}})$.

[f] Clementi, E., McLean, A.D.: Physic. Rev. **133**, A 419 (1964).

[g] Assumed as ~0.04 for bound in analogy with the first row hydride molecules.

[h] Neuman, D., Moskowitz, J.W.: J. chem. Physics **49**, 2056 (1968).

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[j] Foner, S.N., Hudson, R.L.: J. chem. Physics **36**, 2676 (1962).

[k] Difference of zero point energies for $2OH \rightarrow H_2O_2$ from Ref. [c].

[l] Eisenberg, D., Kauzmann, W.: The structure and properties of water. Oxford: Clarendon Press 1969.

them in a systematic manner. A previous experience with calculation on hydrogen peroxyde with limited basis sets has suggested to us the introduction of the *d* functions on the oxygen nuclei; the 4*s* functions with low orbital exponent have been added chiefly in view of the evaluation of some second order observables such as the electric polarizability.

Due to the largeness of the basis used, each attempt to optimize it or to minimize the energy, with respect to the geometry, would result to be prohibitively expensive.

In the Table 2 are reported the calculated values for the total energy in the different configurations and the related values for the barriers, in the hypothesis that the minimum is near to the configuration at 120°.

In the Table 3, we report some guesses for the H.F. limit for hydrogen peroxyde that one can obtain in different ways. One of these consists in subtracting the extimated correlation contributions from the total energy obtained from the experimental data on H_2O_2, while the others utilize also calculated H.F. energies for simple molecules (such as OH and H_2O) that may be considered as fragments of the whole molecule H_2O_2. From the reported data it may be seen that: 1) the difference between the obtained values for the H.F. limit is almost four times the experimental value of the greatest barrier (0.011 a.u.); 2) even in the most favourable hypothesis, the limit is still at 0.066 a.u. from our best result. From this point of view, it is clear that also the previsions that we obtained in this paper, are not free from the fundamental criticism already considered in the introduction. This criticism is *a fortiori* valid for other results (some of which are reported for the sake of comparison in Table 4), that are more distant than ours from the plausible

Table 4. Some previous results for energies and barriers to internal rotation

	Energy (a.u.)			Barriers (kcal/mole)	
	0°	120°	180°	*cis*	*trans*
A[a]	−150.6860	−150.7074[f]	−150.7078	13.7	—
B[b]	−150.7017	−150.7228[f]	−150.7224	13.2	0.32
C[c]	−150.2024	−150.2213	−150.2232	13.1	—
D[d]	−150.2201	−150.2353[f]	−150.2353	9.4	—
E[e,g]	−150.7819	−150.7992	−150.7983	10.9	0.6
F[h]	−150.7689	−150.7910[l]	−150.7906	13.9	0.24
G[i]	−150.8146	−150.8319	−150.8307	10.9	0.72
H[j]			−150.82016[k]	8.34	1.09

[a] Fink, W. H., Allen, L. C.: J. chem. Physics **46**, 2261 (1967).
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[f] Value at 150°.
[g] Optimized geometry.
[h] Davidson, R. B., Allen, L. C.: J. chem. Physics **55**, 519 (1971).
[i] This work.
[j] Dunning, T. H., Winter, N. W.: Chem. Physics Letters **11**, 194 (1971).
[k] Value at 113.7°.
[l] Value at 132°.

H.F. limit. Nevertheless, it is presumable that if a result remains more or less stable when the basis is allowed to grow, it will rest so even at the H.F. limit. As a further check of these considerations, we have carried out two other SCF calculations with partial cancellation of the basis; the results are also reported in Table 2. Even though the incompleteness of these attempts does not allow us to carry out a detailed analysis of the effectiveness of some particular function of the basis in describing the barriers, (an analysis that, in our opinion, has a rather doubtful physical meaning), it is, at any rate, comforting that one could verify a sensible persistence of the results. From our results, together with those previously obtained by several authors (see Table 4), one may reasonably infer that the H.F. calculation for the largest barrier is substantially correct. The remaining difference of 3.86 kcal/mole can by no means, however, be considered negligible; the consideration of the nuclear relaxation should, presumably, permit an improvement of these results. For the lowest one, our results, even though encouraging, do not seem to give a sufficient basis of credibility.

Indeed, one must take into account that, among the previous results for this last quantity, that of Veillard is the only one (as far we know) that shows a discrete agreement with experiments, and this is true only for the version in which the nuclear relaxation is considered.

In a recent paper [8] Davidson and Allen have found for the lowest barrier an improvement of 0.001 a.u. due to the nuclear relaxation and this value is in a good agreement with that of Veillard (0.0009). Presumably the relaxing of the constraint of geometrical rigidity would bring a similar change in our result displacing it to 1.2 kcal/mole, still in a good agreement with experiment. A similar situation seems also to be valid for the main barrier. In conclusion, the nuclear relaxation seems to be crucial for a quantitative agreement to be reached, but not necessary for a qualitative answer on the existence of the barriers and the approximate values for the potential minima.

In Table 5 are reported the forces on the H nuclei in the three configurations examined. These forces are evaluated on the hypothesis that the calculated wave function is a sufficiently good approximation of the H.F. solution, so that for it the Hellmann-Feynman theorem is valid. Due to noticeably complexity of the neglected terms [7] (that are zero only for the true H.F. orbitals), it is not easy to appreciate how such an approximation is suitable. Very plausibly, the error in the case of the oxygen atoms is greater (for the more severe conditions that the SCF orbitals must fulfil near these nuclei), and for that, we do not consider the forces on the oxygen nuclei. If at least the sign of the forces on the protons is exact, from the reported values it may be seen that the effect of the forces is such that the OH bonds tend to be spread apart. This fact shows a qualitative agreement with Veillard

Table 5. Components of the forces at the H nuclei (a.u.)

	x	y	z
0°	−0.00777	0.0	−0.02654
120°	−0.00199	0.00009	−0.01490
180°	−0.00145	0.0	−0.01347

Table 6. Calculated quantities for H_2O_2 molecule

Total energy (Hartree)	−150.83188	−151.6389[a]
$\langle x\rangle$[b] (a.u.)	0.5530	
μ (debye)	1.7356	2.26[c]
θ_{xx}[d] (10^{-26} esu.cm^2)	−1.353	
θ_{zz} (10^{-26} esu.cm^2)	5.476	
Θ[e]	122° 30′	
φ	−30°	
$\langle r^2\rangle$[f] (10^{-16} cm^2)	18.656	
$(e^2qQ^D/h)_{x'x'}$[g,h] (MHz)	−0.138	
$(e^2qQ^D/h)_{z'z'}$ (MHz)	0.3377	
η^D	0.186	
Θ	83° 32′	
$(e^2qQ^{O^{17}}/h)_{x'x'}$[i] (MHz)	0.100	
$(e^2qQ^{O^{17}}/h)_{z'z'}$ (MHz)	−2.849	
$\eta^{O^{17}}$	0.930	
Θ	12° 20′	
φ	−1° 12′	
χ	1° 54′	
$\Omega_{3,0}$[j] (10^{-34} esu.cm^3)	0.074	
$\Omega_{3,1}$ (10^{-34} esu.cm^3)	2.374	
$\Omega_{3,\bar{1}}$ (10^{-34} esu.cm^3)	−0.732	
$\Omega_{3,2}$ (10^{-34} esu.cm^3)	−4.496	
$\Omega_{3,\bar{2}}$ (10^{-34} esu.cm^3)	−0.685	
$\Omega_{3,3}$ (10^{-34} esu.cm^3)	4.980	
$\Omega_{3,\bar{3}}$ (10^{-34} esu.cm^3)	2.108	

[a] See Table 3.

[b] Electronic part.

[c] Landolt-Börnstein: Num. data etc., new series Vol. 4.

[d] Components of the total molecular quadrupole tensor.

[e] Eulerian angles between a system oriented as in Fig. 1, and the principal axes of the tensor. The angles are defined as in Wilson, E.B., Jr., Decius, J.C., Cross, P.C.: Molecular vibrations. McGraw Hill 1955. Only the significant angles are reported.

[f] Electron mean quadratic distance from the center of mass.

[g] The D nucleus is placed in the plane of the Fig. 1.

[h] $Q^D = 0.00277 \cdot 10^{-24}$ e cm^2. Emsley, J.W., Sutcliffe, L.H.: High resolution nuclear magnetic resonance spectroscopy. Oxford: Pergamon Press 1965.

[i] $Q^{O^{17}} = -0.004 \cdot 10^{-24}$ e cm^2. Emsley, J.W., Sutcliffe, L.H.: High resolution nuclear magnetic resonance spectroscopy. Oxford: Pergamon Press 1965.

[j] Spherical components of the total molecular octupole tensor referred to the center of mass as origin.

results [4]; indeed, this author has found that for all the considered values of the rotation angle between 0° and 180°, the value of the total energy is lowered for values of the HOO angle greater than the experimental one. In Table 6, some one electron quantities calculated for the equilibrium configuration of H_2O_2 are reported. The only experimental datum that we found for comparison is the molecular dipole moment, for which the agreement is decidely not good.

The same quantity calculated for the configuration with $\beta = 0°$ is 3.293 D. If the approximation of rigidity of the electronic charge distribution would be valid, one would expect a result of 1.647 D at 120°, a value that is not far from that effectively found.

Insofar as it concerns the electric field gradient, it may be seen that the main direction of the tensor on the proton is practically coincident with the OH bond, while on the oxygen atom it is slightly shifted from the OO bond.

Note. When this paper was completed, we have received the work of Dunning and Winter. Their main results are quoted in Table 4. The agreement of the result for the trans barrier is very good. As in the case of Ref. [4] and [8] the geometry optimization contributes heavily (75% of the total value) to the result for the trans barrier.

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