

Theoretical determination of molecular structure and conformation. I. The role of basis set and correlation effects in calculations on hydrogen peroxide

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Equilibrium structure and barriers to internal rotation of hydrogen peroxide have been accurately determined with the Hartree-Fock method and Rayleigh-Schrödinger perturbation theory using a $(9s5p1d/4s1p)[4s3p1d/2s1p]$ contracted and $(11s6p2d/6s2p)$ uncontracted basis set. Extensive rescaling of the contracted basis accompanied by complete geometry optimization leads to barrier values of 0.7 (*trans*) and 8 (*cis*) kcal/mole. Results obtained with the uncontracted basis indicate an improvement of the barriers to 1.1 and 7.4 kcal/mole comparable to the refined experimental values of Ewig and Harris. Inclusion of correlation does not change the barriers significantly. The latter, however, is necessary to obtain correct equilibrium parameters. The computed bond lengths [$R(\text{OO}) = 1.451 \text{ \AA}$, $R(\text{OH}) = 0.967 \text{ \AA}$] and angles [$\alpha(\text{OOH}) = 99.3^\circ$ and $\theta(\text{HOOH}) = 119.3^\circ$] are in good agreement with experiment while near HF values lead to a false structure [$R(\text{OO}) = 1.390 \text{ \AA}$, $R(\text{OH}) = 0.943 \text{ \AA}$, $\alpha(\text{OOH}) = 102.9^\circ$, $\theta(\text{HOOH}) = 111.2^\circ$]. The importance of optimum scaled polarization functions in the perturbation approach is demonstrated.

I. INTRODUCTION

Although it is widely accepted that single determinant Roothaan-Hartree-Fock (RHF) theory is capable of predicting both molecular structure and molecular conformation of closed shell species, there have been examples of less satisfying and reliable RHF results. Such failures can occur in the case of molecules with vicinal lone pair electrons of which hydrogen peroxide is the most prominent example. Despite the fact that H_2O_2 is the simplest molecule to show internal rotation, it was not until the early seventies that a reasonable account of both the rotational barriers and the equilibrium structure of H_2O_2 could be presented by *ab initio* calculations of the RHF type.¹⁻⁷ In contrast to the situation for ethane where minimal basis set calculations performed for the rigid rotor model are satisfactory, a H_2O_2 calculation must fulfill two criteria: (1) The basis set employed has to be augmented by polarization functions. (2) All structural parameters have to be optimized for both the equilibrium structure and the two rotational transition states. In this respect, the comprehensive RHF study of Dunning and Winter (DW)⁸ gave a state of the art account and provided the best agreement with experimental observations on H_2O_2 thus far obtained.

Nevertheless, significant deviations between the theoretical and the experimental description of H_2O_2 still remain unsolved. Dunning and Winter calculated a *trans* barrier of 1.1 kcal/mole in good agreement with the spectroscopic result while their *cis* barrier of 8.35 kcal/mole, though lower than any rigid rotor value, was still high compared to the observed barrier of about 7 kcal/mole.⁹⁻¹²

Three different reasons have been given recently for this discrepancy. Dunning and Winter⁸ attributed it to inaccuracy in the spectroscopic figures. This argument was contradicted by Howard, Levy, Shull, and Hagstrom.¹³ On the basis of their calculations with strong orthogonal geminals, they concluded that a correlation error may cause the high single determinant result for

the *cis* barrier. Finally, a third opinion was raised by Burton and Markey¹⁴ who used bond functions instead of atom centered polarization functions in their RHF study on H_2O_2 . They argued that the deficiencies of the DW work were caused by basis set limitations rather than correlation effects.

The possibility of basis set errors demands special consideration in view of the second discrepancy between theory and experiment as manifested in the DW work, i. e., the poor agreement of the *ab initio* structural parameters with comparative spectroscopic data.⁹ For example, the RHF OO bond length of 1.39 Å (DW) has to be opposed to an observed length of 1.47 Å.⁹ In addition, the RHF OOH angle of 102° (DW) exceeds the experimental angle by almost 8°.⁹ Ranck and Johansen⁵ who obtained similar structural parameters attributed them to unfavorably scaled polarization functions. After all, Veillard's augmented basis set calculation¹ gave a OO distance almost identical with the spectroscopic one as did the bond function calculations of Burton and Markey.¹⁴

The situation, however, becomes confusing when the structural findings of the DW work are viewed against the background of three additional facts: (1) A short OO bond distance is consistent with near HF calculations on first-row diatomic molecules.¹⁵ It probably indicates the lack of electron correlation inherent in the HF model.¹⁶ (2) None of the H_2O_2 investigations so far published¹⁻⁸ provide an OOH angle significantly lower than 99°. RHF calculations on water,^{17,18} however, lead to a theoretical bond angle within 1.5° of the observed value.^{19,20} (3) A discrepancy in the OOH angle should be coupled with a similar discrepancy in the dihedral angle.²¹ Nevertheless, Dunning and Winter consider the accuracy of their computed equilibrium dihedral angle satisfactory.⁸

The purpose of this paper is to check on this controversy by analyzing the three different arguments, namely basis set deficiencies, correlation errors or inaccuracy of experimental figures. In Sec. III we start with

a short explanation of the rotational behavior of hydrogen peroxide given in molecular orbital terms. A review of the criteria for adequate basis set descriptions of skewed, *trans*, and *cis* H₂O₂ is added. In the succeeding section the results of minimal, extended, and augmented basis set calculations are discussed in the light of these criteria and on the basis of the Mulliken population analysis. The possibility of correlation errors is checked in Sec. V by the aid of the Rayleigh-Schrödinger perturbation theory.²² Then, in Sec. VI the effects of extensive rescaling on both RHF and correlation corrected results are reported. Finally, in Sec. VII the experimental observations on H₂O₂ will be critically discussed in view of our theoretical results.

II. DESCRIPTION OF NUMERICAL PROCEDURES

Quantum mechanical methods. The *ab initio* calculations reported in this work are based on standard self-consistent field molecular orbital theory and on the Rayleigh-Schrödinger (RS) perturbation theory. Within the approximations of the single-determinant Hartree-Fock (HF) method the molecular orbitals (MO) are expanded as linear combinations of basis functions. Solution of the Roothaan-Hall equations²³ for a fixed nuclear configuration yields the expansion coefficients and, thereby, the RHF ground-state wavefunction and energy.

In order to correct single determinant results for correlation effects, we follow a procedure first described by Møller and Plesset (MP).²⁴ In the MP approach the correct Hamiltonian is expressed by the sum of the Fock operators $\hat{F}^{(i)}$ and a perturbation operator $\hat{\Gamma}$:

$$\hat{H} = \sum_i \hat{F}^{(i)} + \hat{\Gamma} - G. \quad (1)$$

In this expression the constant G is introduced for the reason that the eigenvalue of the operator $\hat{\mathcal{F}} = \sum_i \hat{F}^{(i)}$ which is equal to the orbital energy $E^{\text{orb}} = \sum_i \epsilon_i$, counts the electron interaction energy twice. With the standard expressions for \hat{H} and $\hat{F}^{(i)}$ the MP perturbation operator is given by

$$\hat{\Gamma} = \frac{1}{2} \sum_{i \neq j} \sum V(r_{ij}) - \sum_i (\hat{J}^{(i)} - \hat{K}^{(i)}) + G, \quad (2)$$

where $\hat{J}^{(i)}$ and $\hat{K}^{(i)}$ have the usual meaning of total Coulomb and total exchange operator.

If the HF energy and the HF wavefunction are taken as the zeroth-order energy $E_0^{(0)}$ and zeroth-order wavefunction $\Phi_0^{(0)}$ of the ground-state, corrections of first, second, and higher orders can be evaluated by standard RS perturbation theory,²² thus giving various approximations to E_0 and Φ_0

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots \quad (3)$$

$$\Phi = \Phi^{(0)} + \Phi^{(1)} + \Phi^{(2)} + \dots$$

Since we are confining ourselves to the ground-state the subscript is dropped in Eq. (3). To evaluate (3) a set of eigenfunctions $\Phi_s^{(0)}$ of $\hat{\mathcal{F}}$ is constructed from $\Phi^{(0)}$ by replacing occupied spin orbitals ψ_i by virtual spin orbitals ψ_a . This leads to singly, doubly, and higher substituted determinants Φ_i^a , Φ_{ij}^{ab} , etc., which are used to de-

termine the matrix elements of the MP operator. As was demonstrated by Møller and Plesset²⁴ the first-order energy $E^{(1)}$ calculated in this way vanishes, i.e., the HF energy is accurate up to second order. Further, it was shown that the second order correction $E^{(2)}$ is readily established according to

$$E^{(2)} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{|\langle \Phi^{(0)} | \hat{\Gamma} | \Phi_{ij}^{ab} \rangle|^2}{E_0^{(0)} - E_{ij}^{ab}} \quad (4)$$

where

$$E_{ij}^{ab} = \epsilon_a + \epsilon_b + \sum_{k \neq i, j} \epsilon_k - G. \quad (5)$$

In Eq. (4) only doubly substituted determinants appear. Matrix elements including determinants Φ_i^a vanish because of Brillouin's theorem²⁵ as do those including triply and higher substituted determinants because (2) contains only one- and two-electron operators. The final form of $E^{(2)}$ is found by applying (5) and the familiar Slater rules:

$$E^{(2)} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{|\langle ij | ab \rangle - \langle ij | ba \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (6)$$

The evaluation of (6) demands only a partial transformation of two-electron integrals over basis functions to those over molecular orbitals.²⁶ Hence, the expression (6) provides a simple way to correct the HF energy for correlation effects.²⁷

Basis sets. Various augmented basis sets of Gaussian type functions (GTF) have been employed in this work. Calculations of Sec. VI were performed by using Dunning's (9s5p/4s) [4s3p/2s]²⁸ contracted basis set.²⁹ This was augmented by a set of six second-order Gaussians ($x^2, y^2, z^2, xy, yz, xz$) for oxygen and a set of 2p Gaussians (x, y, z) for hydrogen. Because of computational reasons all second-order Gaussians were retained, thus leading to an equivalent of five 3d and a single 3s GTF ($x^2 + y^2 + z^2$). Exponents of polarization functions have been optimized both at the HF and RS-MP level of theory. In addition, complete rescaling of basis functions were performed (see Tables VII and IX) from which individual Gaussian exponents ζ^G were obtained according to

$$\zeta^G = \zeta^2 \alpha \quad (7)$$

(ζ : scale factor; α : exponent of a primitive GTF). The largest basis set used in this work is an (11s6p/6s) uncontracted basis of GTF's taken from a tabulation of HF optimized functions due to van Duijneveldt.³⁰ It was augmented by two sets of 3d functions ($\zeta_{3d}^G = 1.50$ and 0.35^{30}) and two sets of hydrogen p functions ($\zeta_{2p}^G = 1.40$ and 0.25^{30}), thus leading to a (11s6p2d/6s2p) basis.

The implications of smaller basis sets have been demonstrated with the sets A, B, C, and D taken from the work of Pople. The smallest basis is the familiar STO-3G minimal basis.³¹ The second is a (8s4p/4s) [3s2p/2s] split valence basis set.³² Basis sets C and D provide a better description of the inner shell s orbital of oxygen by using six rather than four contracted GTF's. In addition, basis C possesses one set of 3d GTF's while basis D has in addition a set of hydrogen 2p polarization functions. Accordingly, the notation of

basis *C* and *D* is $(10s4p1d/4s) [3s2p1d/2s]$ and $(10s4p1d/4s1p) [3s2p1d/2s1p]$. Standard exponents of $\zeta_{3d}^C(\text{O}) = 0.80$ and $\zeta_{2p}^C(\text{H}) = 1.10$ are used in *C* and *D* throughout.³³

Optimization technique. Energy minimization with regard to structural parameters and scale factors of basis functions were performed with an improved version of the *complementary Davidson-Fletcher-Powell* (DFP) method.^{34,35} Energy derivatives were calculated with a finite-difference technique³⁶ starting with increments of 0.01 Å for bond lengths, of 1° and 2.5° for angles and of 0.001, 0.01, and 0.02 for scale factors. Convergence was achieved when changes in energy were less than 3×10^{-5} hartree, and the reduced norm of the gradient was lower than 0.01.³⁷ Structural parameters thus obtained are accurate to 0.002 Å and 0.2°. The accuracy of scale factors amounts to 0.001. During scale factor optimizations single checks were necessary to distinguish between local and global minima in basis function space. It turned out that for the *trans* form the scale factors of Ref. 8 provide a good initial guess to get within three cycles to the global minimum of the energy where one cycle includes the evaluation of the energy gradient and a parabolic fit of the energy hypersurface in the direction of the negative gradient.

Computer programs: All calculations have been performed with the program package COLOGNE 76 on a CDC CYBER 76. COLOGNE 76 contains the integral package of GAUSSIAN 70.³⁸ An optimization package, the SCF part, and routines for the RS-MP calculations have been written by the author.

III. EXPLANATION OF ROTATIONAL BARRIERS

The first proposal for a quantum mechanical description of the rotational behavior of hydrogen peroxide was given as early as 1934 by Penney and Sutherland³⁹ on the basis of a valence bond study. These authors anticipated that the potential function $V(\Theta)$ ⁴⁰ would depend on two components, namely the repulsion of the oxygen lone pair electrons and the interactions of the OH bond dipole moments. On the assumption that the lone pairs are located in the O $2p$ orbitals maximum repulsion was expected to occur with a periodicity of π at $\Theta = 0^\circ$ and $\Theta = 180^\circ$, thus giving rise to a Fourier component $V_2 \cos(2\Theta)$. On the other hand, bond dipole moment interaction should possess a maximum for the *cis* form and minimum for the *trans* form which can be described by a Fourier term of $V_1 \cos(\Theta)$. A favorable interplay of these two components was considered to be the cause of the extra-stability of skewed H_2O_2 and, thereby, the rotational barriers at $\Theta = 0^\circ$ and $\Theta = 180^\circ$.

The arguments of Penney and Sutherland are still valid in modern MO theory, though the description of the various stabilizing and destabilizing effects has somewhat changed. Radom, Hehre, and Pople⁴¹ found a general tendency of lone pair orbitals to be coplanar with adjacent polar bonds. Under these circumstances lone pair delocalization in the polar bond takes place, leading to an overall stabilization of a molecule like H_2O_2 in its skewed form. In line with this observation is the interpretation of the overlap populations of skewed H_2O_2 as

given by Veillard¹: Due to a hyperconjugative interaction between the OH bond and the vicinal lone pair, some π -bond character is added to the OO bond, thus stabilizing the skewed form in relation to the planar forms. According to Veillard the *cis* barrier is mainly affected by strong H, H antibonding which may be regarded as the quantum chemical analogue of bond eclipsing in rotor molecules. Therefore, the analytical form of $V(\Theta)$ ³⁹ is corrected by a third Fourier term, namely $V_3 \cos(3\Theta)$.

More or less successful attempts to attribute the "underlying cause" of the H_2O_2 barriers to the interaction of attractive and repulsive forces,^{1,3} to the contributions of exchange energy and orbital orthogonality⁴² or to the special role of localized charge distributions⁴³ have also been put forward. However, all these explanations are similar to the approach of Pople or Veillard in the way that they all demand an explicit knowledge of the H_2O_2 wavefunction, i. e. calculations of some sort are the prerequisite of their predictive ability.

A way to avoid the calculation of the wavefunction is offered by the perturbational molecular orbital (PMO) theory.⁴⁴ Within the PMO description H_2O_2 is considered as the result of the combination of two hydroxyl radicals. Orbital interactions between the two fragments decide on the most stable conformation. This is outlined in Fig. 1.

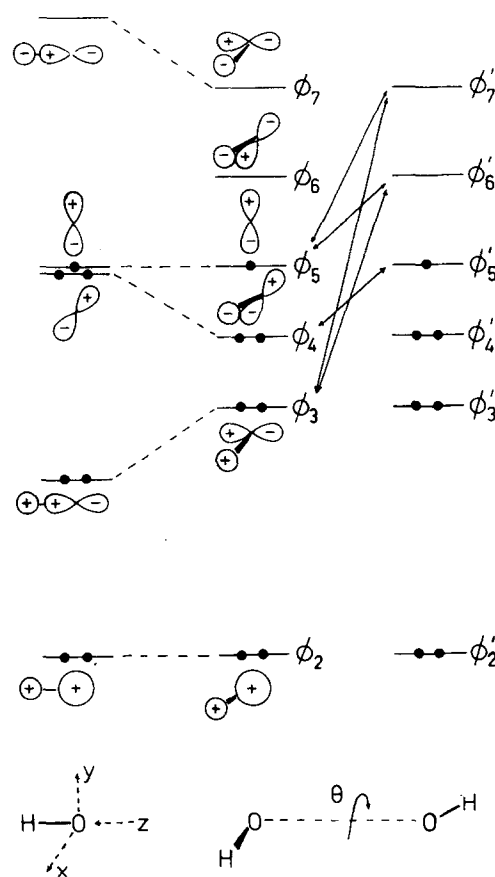


FIG. 1. The interaction of OH group orbitals in *cis*, skew, and *trans* hydrogen peroxide (only one set of interaction lines is shown). Notice that the OH group orbitals are not identical with the MO's of the hydroxyl radical depicted on the left.

Walsh⁴⁵ has already noted that linear H_2O_2 should be characterized by the unfavorable electron configuration $\dots 1\pi_u^4 1\pi_g^4$. Distortions towards a bent H_2O_2 geometry lower the energy due to a favorable mixing of the inplane π_g orbital with the H 1s orbitals. Our PMO analysis is based on Walsh's result in so far as OH group orbitals (GO) are used rather than the OH valence MO's depicted on the left of Fig. 1. The GO's ϕ_2 to ϕ_7 can be constructed from the corresponding H_2O MO's by removing the 1s contributions of the second H atom.⁴⁶ Stabilizing or destabilizing interactions with the second set of GO's ϕ'_2 to ϕ'_7 which can be qualitatively measured by the relative magnitude of their overlap decide the preferred position of OH bonds in the final H_2O_2 . The following conclusions with regard to the relative stabilities of skewed, *trans*, and *cis* H_2O_2 can be drawn from Fig. 1:

(1) *Stabilization of the skew form.* The overlap between orbitals ϕ_5 and ϕ'_5 can be in-phase and out-of-phase for a planar form while it completely vanishes for an orthogonal conformation. No distinction with regard to relative stabilities is possible. A preference of skewed H_2O_2 , however, will result from interactions $\phi_5-\phi'_6$ and $\phi_4-\phi'_5$. There, bonding overlap between the oxygen atoms becomes possible for $0^\circ < \Theta < 180^\circ$ with a maximum at $\Theta = 90^\circ$, thus leading to strengthening of the OO bond and, hence, to overall stabilization. This effect will be enhanced by interactions $\phi_5-\phi'_7$ and $\phi_3-\phi'_5$ due to overlap of the oxygen p orbital with a vicinal hydrogen 1s orbital. Besides a shorter OO bond length a somewhat reduced OOH angle can be expected for skewed H_2O_2 .

(2) *Stabilization of the trans form.* This is provided by those orbital interactions which are H, H antibonding at all rotational angles, for example $\phi_3-\phi'_6$, $\phi_3-\phi'_7$, etc. While the antibonding effect will be considerable in the *cis* form it possesses fewer destabilizing consequences in the *trans* form where absolute overlap is much smaller in magnitude. The differences in the H, H overlap will influence the size of the OOH angle in the planar forms. If the molecule tries to avoid strong H, H antibonding in its *cis* conformation by widening of the bond angle, a decrease of $1s-2p_x$ overlap in ϕ_4 may weaken the OH bond and, hence, further destabilize *cis* H_2O_2 with respect to *trans* H_2O_2 .

With the aid of the PMO approach not only the relative stabilities of skewed, *trans*, and *cis* H_2O_2 become evident but also the requirements of an adequate basis set description of the various overlap interactions. It seems that with a basis set of given size, a theoretical recording of the *trans* form is less critical, but more critical for the skewed form. In the latter case great flexibility is demanded from basis set functions in order to describe stabilizing overlap between the oxygen atoms. The overlap will be of π -type characterized by high anisotropy due to its extension over three atomic centers. Basis functions with the right nodal, magnitudal, and directional properties are important.

At first sight, the description of the *cis* form seems to produce no problems. But the expected angle widen-

ing due to antibonding overlap may cause an unbalanced decrease of the OH overlap, if a rigid basis set is employed. Again, flexible basis set functions especially for the O atoms are necessary to allow a reasonable description of the OH bonds in a more open, less antibonding form of *cis* H_2O_2 .

IV. BASIS SET EFFECTS

The variety of basis sets used in the past for RHF calculations on H_2O_2 can be approximately grouped into four categories: (1) Minimal basis sets of single- ζ -quality, (2) Extended basis sets of double- or multiple- ζ -quality, (3) Partially augmented basis sets with polarization functions just for the O or H atoms and (4) Fully augmented basis sets with polarization functions for both the O and H atoms.¹⁻⁸ The classifications (1)-(4) is consistent with a stepwise enhancement of the flexibility of the basis which leads not only to quantitative but also to qualitative improvements in the description of H_2O_2 .

In view of the PMO analysis of the preceding section, the failure of type 1 and type 2 basis set calculations is not surprising. Most of the recent work on H_2O_2 has been aimed at stressing the role of polarization functions in the description of the skew form and its *trans* barrier height. Less attention, however, has been paid to the effects of basis set limitations on the *cis* barrier. It was noted¹ that augmented basis sets lead to a lowering of the *cis* barrier. Yet no explanation of this result was offered. Similarly, the superiority of some basis sets in predicting the OO and OH bond lengths has remained unexplained. In order to clear up this situation and to deal with arguments given by Burton *et al.*¹⁴ we have compared barriers and geometries obtained with basis sets A to D which can be considered as simple representatives of categories (1)-(4). Although basis set A and basis set B results are already in the literature⁴⁷ calculations have been repeated to obtain overlap populations for optimized structures. With basis sets C and D complete structure determinations for *cis*, *trans*, and skewed H_2O_2 have been performed.

Table I presents absolute and relative energies of the three optimized structures, Table II the corresponding geometrical parameters and Table III dipole moments, gross atomic populations and overlap populations obtained with basis sets A to D. Only relative changes of population values can be discussed because of the deficiencies of the Mulliken analysis.⁴⁹ Having this in mind the following conclusions can be drawn from the data in Tables I, II, and III:

Minimal basis sets (Basis A). Due to their small size and rigidity these basis sets cannot provide sufficient directional flexibility. No extra overlap in the skewed form is possible. In addition, an OOH angle close to 90° is necessary to provide effective OH overlap. The tendency to widen the OOH angle in the *cis* form in order to decrease H, H-antibonding overlap cannot be adequately described. Obviously, this leads to a low or lacking *trans* barrier, a high *cis* barrier, long OH bonds, small OOH angles and an equilib-

TABLE I. Absolute and relative energies of hydrogen peroxide obtained with different basis sets at the Roothaan-Hartree-Fock level.

Conformation	Basis A ^a STO-3G	Basis B ^{b,c} [3s2p/2s]	Basis C ^c [3s2p1d/2s]	Basis D ^c [3s2p1d/2s1p]
Absolute energies (hartree)				
skew	-148.76500	(-150.55894) ^d	-150.76478	-150.77696
trans	-148.76488	-150.55991	-150.76328	-150.77557
cis	-148.75043	-150.54161	-150.75020	-150.76325
Relative energies (kcal/mole)				
skew	0.00	(0.60) ^d	0.00	0.00
trans	0.08	0.00	0.94	0.87
cis	9.14	11.48	9.15	8.60

^aReference 47.^cThis work.^bReference 41.^dCalculated for $\Theta = 120^\circ$. No minimum for skewed H₂O₂ obtained.

rium dihedral angle close to 180° (Tables I and II; see also Table II of Ref. 8). The minimum at $\Theta = 125^\circ$ obtained with basis A is clearly fortuitous.

Less plausible is the reason for the short OO distance. From the low dipole moment and the gross atomic populations (Table III) found with basis A we conclude that the rigidity of the basis does not allow sufficient charge transfer from the hydrogens to the oxygens. Consequently, repulsion between O atoms is low and allows significant OO bond length shortening in order to enhance overlap. This, in turn, raises the antibonding H, H overlap of the *cis* form and, accordingly, leads to further destabilization.

Basis sets of multiple- ζ -quality (Basis B). Although basis B is still moderate in size and flexibility, it allows the necessary charge transfer from oxygen to hydrogen because of its splitting in inner and outer valence shell functions. According to the Mulliken population analysis (Table III) the diffuse 1s functions of the hydrogens are strongly depopulated while the reverse is the case for the outer oxygen functions. There is an increase in charge separation by about 100% with regard to basis A.

Repulsion of the negative charge residing in the outer valence region of the O atoms obviously cannot be counterbalanced by sufficient enlargement of OO overlap. Thus the result is a significant lengthening of the OO distance accompanied by a shortening of the OH bonds. Although the H₂O₂ distances now are more in agreement with experiment,⁹ the true HF value of $R_e(\text{OO})$ should be shorter than 1.47 Å. Any enhancement of the basis will offset the charge separation effect in part by improved OO overlap. Therefore, coincidence with observed H₂O₂ bond lengths is accidental for basis B. Its deficiencies are clearly manifested by its conformational predictions. Due to the large OH polarity any rotational distortion of the *trans* form leads to strong destabilizing bond dipole moment interactions. Again, no sufficient stabilization of skewed H₂O₂ can be provided by the basis. Although the flexibility of the basis now allows an opening of the OOH angle, the dominance of charge repulsion leads to a *cis* barrier which is 2.3 kcal/mole higher than the one obtained with basis A. This difference is reduced by 1 kcal/mole, if a more flexible type 2 basis is used.⁸

We conclude that for type 2 basis set calculations the

TABLE II. Structural parameters of hydrogen peroxide as determined by RHF calculations with basis sets A to D (bond lengths in Å; angles in degrees).

Conformation	Parameter	Basis A ^a STO-3G	Basis B ^{b,c} [3s2p/2s]	Basis C ^c [3s2p1d/2s]	Basis D ^c [3s2p1d/2s1p]
skew	R(OH)	1.001	0.956	0.946	0.946
	R(OO)	1.396	1.460	1.396	1.396
	$\alpha(\text{OOH})$	101.1	102.3	102.3	102.3
	$\Theta(\text{HOOH})$	125.3	(120.0) ^d	116.3	116.3
trans	R(OH)	0.999	0.955	0.949	0.945
	R(OO)	1.402	1.468	1.406	1.405
	$\alpha(\text{OOH})$	99.8	100.8	100.6	100.8
cis	R(OH)	1.001	0.957	0.949	0.945
	R(OO)	1.406	1.465	1.404	1.402
	$\alpha(\text{OOH})$	104.9	107.9	106.7	107.0

^aReference 47.^cCalculated for $\Theta = 120^\circ$. No minimum for skewed H₂O₂ obtained.^bReference 41.^cThis work.

TABLE III. Results of Mulliken population analysis and calculated dipole moments of *cis*, skew, and *trans* H₂O₂ obtained with the basis sets A to D.

Conformation	Population	Basis A STO-3G	Basis B ^a [3s2p/2s]	Basis C [3s2p1d/2s]	Basis D [3s2p1d/2s1p]
Gross populations					
<i>cis</i>	O atomic	8.1777	8.4102	8.4463	8.3482
	2s _i + 2p _i		3.5348	3.7423	3.7333
	2s ₀ + 2p ₀		2.8799	2.6143	2.5497
	3d			0.0941	0.0695
	H atomic	0.8223	0.5898	0.5537	0.6518
	1s _i		0.5142	0.4756	0.5024
	1s ₀		0.0756	0.0781	0.1067
	2p				0.0426
skew	O atomic	8.1926	(8.4358)	8.4619	8.3653
	2s _i + 2p _i		(3.5394)	3.7467	3.7366
	2s ₀ + 2p ₀		(2.9008)	2.6258	2.5645
	3d			0.0939	0.0686
	H atomic	0.8074	(0.5642)	0.5381	0.6347
	1s _i		(0.5038)	0.4695	0.4962
	1s ₀		(0.0604)	0.0686	0.0972
	2p				0.0413
<i>trans</i>	O atomic	8.1931	8.4435	8.4681	8.3710
	2s _i + 2p _i		3.5394	3.7460	3.7359
	2s ₀ + 2p ₀		2.9085	2.6341	2.5720
	3d			0.0925	0.0675
	H atomic	0.8068	0.5565	0.5319	0.6290
	1s _i		0.5006	0.4665	0.4935
	1s ₀		0.0559	0.0654	0.0939
	2p				0.0415
Overlap populations ^b					
<i>cis</i>	OO	0.3338	0.1088	0.1318	0.1234
	OH	0.4806	0.4642	0.4994	0.5988
	HH	-0.0268	-0.0096	-0.0160	-0.0194
skew	OO	0.3374	(0.1093)	0.1524	0.1378
	OH	0.4850	(0.4916)	0.5166	0.6156
	HH	0.0082	(0.0037)	0.0034	0.0032
<i>trans</i>	OO	0.3348	0.1020	0.1414	0.1278
	OH	0.4854	0.4988	0.5196	0.6198
	HH	0.0086	0.0060	0.0072	0.0074
Dipole moments (debye)					
<i>cis</i>		2.72	4.12	3.54	3.50
skew		0.62	(2.20)	1.95	1.92

^aValues in parenthesis obtained for $\Theta = 120^\circ$.^bOO and OH bonded, HH nonbonded.

description of rotational barriers is as incorrect as in a minimal basis set treatment. With regard to structure predictions there seems to be a relationship between the OO distance and the size of the basis: The smaller a type 2 basis is, the more the charge separation effect outweighs the stabilizing overlap, the longer the bond length is and the better the seeming agreement with the experimental value is.⁴⁸

Partially augmented basis sets (Basis C). The role of oxygen centered polarization functions in an adequate description of skewed H₂O₂ and its *trans* barrier is well documented¹⁻⁸ and needs no further consideration here. Therefore, our analysis will be confined to the lowering of the *cis* barrier height and the shortening of bond dis-

tances obtained with basis C. While the gross atomic populations (Table III) again indicate a strong separation of charge, even stronger than the one predicted by basis B, increased overlap populations indicate a significant improvement in the stabilizing overlap. The gain in the total overlap population⁴⁹ amounts to more than 0.1 and is largest for the *cis* form due to a 0.04 increase of the OH overlap population. It is obvious that a deterioration of OH overlap caused by necessary angle widening in the *cis* form is now partially counterbalanced by the directional flexibility of basis C. Hence, less destabilization of the *cis* form and a lower *cis* barrier result.

Although changes in overlap certainly influence the calculation of bond distances, nevertheless, a reduction

of the OO length by 0.06 Å is surprising, especially in view of the calculated gross atomic populations. We have already mentioned that charge residing in the outer valence shell functions of the O atoms leads to strong OO repulsion and bond lengthening. This charge can be dismantled by shifting it either to the region of bonding OH or OO overlap or to the inner valence shell area. Basis C provides not only the first possibility (improvement of overlap due to polarization functions) but also the second by using six rather than four contracted GTF's for the 1s(O) orbital. In this way, the inner valence functions are somewhat detached from the region of the 1s orbital. They expand more into surrounding space (lower ζ -values) thus enabling basis C to store more charge in the inner valence shell region than basis B does. This effect is reflected by the gross populations of inner and outer valence GTF's as well as the lowering of the dipole moment. In consequence, it leads to reduced OO repulsion and a shorter OO distance. Actually, this redistribution of charge is typical for an improvement of type 2 basis sets and explains the relationship between OO bond lengths and basis set size mentioned above.

Fully augmented basis sets (Basis D). Inclusion of p functions centered at the H nuclei provokes a further lowering of the *cis* barrier. Destabilizing charge in the outer O functions can now be more strongly shifted in the zone of OH overlap. As there is an equal distribution of overlap populations among bonded atoms in the Mulliken population analysis,⁴⁹ it seems as if the H atoms get some of the lost charge back donated by virtue of their p functions. Although this effect has some similarity to the bonding in transition-metal complexes, there is no real physical relevance to it. We conclude that the p functions on hydrogen provide a further improvement of the description of the *cis* form, the form which is most sensitive to charge transfer and charge repulsion. As has been demonstrated in Refs. 2 and 3 augmentation of a type 2 basis set with hydrogen polarization functions may also effect some extra-stabilization of the skew form in the way that the $2p$ GTF's take over part of the role of the $3d$ GTF's. In a type 4 basis set, however, their real importance is reflected by the lower *cis* barrier height.

In view of the dependence of calculated barrier values and geometries on the type of the basis, the argument of Burton *et al.*,¹⁴ that carefully chosen basis sets augmented by bond functions will lead to theoretical values close to experiment has to be rejected. Results of Ref. 14 are characteristic for a type 2 basis set calculation with insufficient overlap but strong charge separation. Although the inclusion of bond functions stabilizes the skew form, the basis set employed in Ref. 14 is neither capable of shifting charge into the inner valence shell region (improvement of the basis by additional inner shell or inner valence functions) nor into the OH bond region ("back-donation" effect due to $2p(\text{H})$ functions). Exaggerated charge repulsion consequently leads to a high *cis* barrier (9.3 kcal/mole) a long OO distance (1.48 Å) and a high dipole moment (2.5 Debye).¹⁴ An improvement of the sp basis would certainly reduce these values, especially the OO distance. In this connection, recent results of Ryan and Todd⁵⁰ are illustrative. In their study on H_2O_2 , these authors have used lone-pair functions which also lead to a skew minimum of $V(\Theta)$. Again, the calculated *cis* barrier and the structural parameters are typical for the underlying sp basis. As the latter is more flexible than the one of Ref. 14 less charge repulsion, a lower dipole moment and a much shorter OO distance is evaluated. Doubtless, near HF calculations with or without bond (or lone-pair) functions will lead to a short OO bond length somewhat below 1.40 Å. In this respect, we consider the value obtained by Veillard¹ as erroneous. Our argument is based on the fact that the OO overlap populations of Ref. 1 are all negative which is unrealistic and indicative of a basis set error. Also, the high *cis* barrier is atypical for type 4 basis set calculations. One probable source of error may be attributed to the fact that only $3d_{xz}$ and $3d_{yz}$ GTF's have been employed each with a high exponent of 1.5. Incomplete optimization may also have influenced final results.

V. CORRELATION EFFECTS

In order to make an assessment of possible correlation errors⁵¹ caused by the restrictions of the HF model we present the results of second order perturbation calculations in Tables IV (energies) and V (structures).

TABLE IV. Absolute and relative energies of hydrogen peroxide as calculated by second order perturbation theory using the Møller-Plesset approximation.

Conformation	Basis A STO-3G	Basis B [3s2p/2s]	Basis C [3s2p1d/2s]	Basis D [3s2p1d/2s1p]
Absolute energies (hartree)				
skew	(-148.84537) ^a	(-150.82166) ^a	-151.13492	-151.15709
trans	-148.84584	-150.82313	-151.13396	-151.15613
cis	-148.83169	-150.80436	-151.14308	-151.14308
Relative energies (kcal/mole)				
skew	(0.29) ^a	(0.92) ^a	0.00	0.00
trans	0.00	0.00	0.60	0.60
cis	8.88	11.77	9.43	8.79

^aCalculated for $\Theta = 120^\circ$. No minimum obtained for skewed H_2O_2 .

TABLE V. Structural parameters of hydrogen peroxide as determined by second order perturbation theory using the Møller–Plesset approximation (bond lengths in Å; angles in degrees).

Conformation	Parameter	Basis A	Basis B	Basis C	Basis D
		STO-3G	[3s2p/2s]	[3s2p1d/2s]	[3s2p1d/2s1p]
skew	R(OH)	1.027	0.988	0.975	0.967
	R(OO)	1.443	1.560	1.466	1.464
	α (OOH)	98.8	97.9	98.7	98.7
	Θ (HOOH)	(120.0) ^a	(120.0) ^a	120.6	119.4
trans	R(OH)	1.026	0.987	0.975	0.967
	R(OO)	1.452	1.566	1.478	1.476
	α (OOH)	97.1	96.3	97.2	97.2
cis	R(OH)	1.028	0.993	0.976	0.968
	R(OO)	1.458	1.562	1.474	1.472
	α (OOH)	102.5	103.6	104.0	103.7

^aCalculated for $\Theta = 120^\circ$. No minimum obtained for skewed H₂O₂.

Though perturbational calculations with limited basis sets are of dubious value, we have included results obtained with small basis sets A and B for reasons of comparison. From inspection of Tables IV and V three general statements can be made: (1) Going from basis A to D the relative changes in barrier values and equilibrium structures remain the same. (2) The structural parameters indicate an overall improvement compared with RHF results. (3) A slight change for the worse has occurred with regard to the barrier values.

As can be seen from Tables II and V improvement of H₂O₂ distances is most striking. This is caused by double-excitations (see Eqs. (4) and (6)) to ψ_a and ψ_b MO's which have the right nodal properties to allow for left-right correlation in the OO and OH bonds. The statefunctions Φ_{ij}^{ab} corresponding to these excitations interact with the ground state function $\Phi^{(0)}$ most strongly at bond distances characteristic for bond dissociation. Therefore, a significant contribution of the second order energy to the total energy demands an increase of the bond lengths which is cushioned by the inevitable deterioration of the HF energy. The optimum bond distances at the RS-MP level though lengthened due to left-right correlation still reflect basis set effects. As improvements of the basis will lead to a lowering of orbital energies ϵ_a and ϵ_b as well as to a better overlap between functions Φ_{ij}^{ab} and $\Phi^{(0)}$ it is clear that for limited basis sets like B considerable OO and OH lengthening far beyond experimental values is necessary while for augmented basis sets like C and D H₂O₂ lengths are in accordance with experimental results. Similar observations have already been made in CI-studies.⁵²

The inclusion of electron correlation also improves the calculated OOH angles by reducing them to lower values. This may be partially connected with the longer atom-atom distances, partially with the allowance for angular correlation. Both effects decrease H, H repulsion and, thereby, bond angles. The 3°–4° increase of the equilibrium dihedral angle obtained at the RS-MP level should also be noted.

In order to analyze the correlation contribution to the barrier values we have split the calculated second order

correlation energies into intra- and interpair portions which are listed in Table VI for basis C and D.

Correlation dependent stabilization or destabilization of skewed H₂O₂ with regard to its *cis* and *trans* forms is generally small, with a tendency to become even smaller for the more flexible basis sets. The partitioning of the correlation contribution, however, indicates significant effects of opposite sign: The calculated relative intra- and interpair energies though larger than the *trans* barrier are well balanced for each of the three conformations. The former favor the *cis* form by more than 3 kcal/mole while the latter stabilize the skew form by a similar amount. Intra- and interpair contributions to the energy of the *trans* form are 1 kcal/mole smaller but with a somewhat larger net effect on the barrier height.

Again, this result can be explained on the basis of overlap and charge separation. The additional overlap in the orthogonal form causes intensified interactions

TABLE VI. Absolute and relative contributions of second order correlation energies $E^{(2)}$.^a

Basis	$E^{(2)}$	<i>cis</i>	skew	<i>trans</i>
Absolute correlation energies (hartree)				
C [3s2p1d/2s]	total	-0.37426	-0.37459	-0.37540
	intra	-0.07827	-0.07238	-0.07536
	inter	-0.29599	-0.30222	-0.30004
D [3s2p1d/2s1p]	total	-0.38410	-0.38418	-0.38487
	intra	-0.07963	-0.07369	-0.07680
	inter	-0.30447	-0.31049	-0.30807
Relative correlation energies (kcal/mole)				
C	total	0.21	0.00	-0.50
	intra	-3.70	0.00	-1.87
	inter	3.91	0.00	1.37
D	total	0.06	0.00	-0.43
	intra	-3.72	0.00	-1.95
	inter	3.78	0.00	1.52

^aAbbreviations intra and inter are standing for intrapair and interpair correlation energy.

between lone-pair and OH bond electrons, thus enhancing interpair correlation. On the other hand, strong charge repulsion in the *cis* form shifts charge into the inner valence region. The inner valence shell functions take a larger share in the construction of the occupied MO's which, consequently, appear to be more constrained to the area of the nuclear framework in the *cis* form than in the skew or *trans* form. Therefore, intrapair correlation is largest in the *cis* form.

Our results cast light on the statement of Shull and coworkers¹³ that correlation may play a role by lowering the energy of the *cis* barrier. We find their predictions with regard to intrapair correlation energies correct, but we cannot confirm the assumed constance of interpair correlation energies. If correlation should play a role, its effects on the H₂O₂ barriers are, certainly, of an order of magnitude smaller than stated in Ref. 13. Further proof for this result will be presented in Sec. VI.

VI. CALCULATIONS WITH OPTIMUM BASIS SETS

In the DW study⁸ on H₂O₂ it is shown that within the HF approximation an accurate account of the *trans* barrier is possible if the basis set is well-chosen and geometry optimization is performed at all rotational angles. The polarization functions of the [4s3p1d/2s1p] basis employed in Ref. 8 were optimized for *trans* H₂O₂ and, then, used with the same exponents for all other H₂O₂ conformations. This procedure ought to be, of course, of some disadvantage for the description of *cis* H₂O₂. There, as was mentioned above, the H 2p functions are of special significance for the dismantling of charge held by the O atoms. To that purpose optimum overlap with the O functions is a basic requirement, which may be achieved by rescaling of the basis set for the *cis* form. After all, the *cis* barrier computed by Dunning and Winter still exceeds the experimental value by 1.3 kcal/mole.⁸⁻¹²

As preliminary calculations seemed to confirm this assumption, we evaluated optimum scale factors for *cis* H₂O₂. First, the exponents of the 3d(O) and the 2p(H) set as well as the two scale factors of the hydrogen s functions were optimized using the geometry of Ref. 8. Subsequently, a possible coupling between these parameters and the scale factors of the remaining O functions was investigated. This turned out to be important with regard to the outer oxygen s and p GTF's. Hence, the optimization was repeated including all scale factors of the basis set but the one of the 1s(O) function. Finally, the structure of *cis* H₂O₂ was redetermined for the computed optimum scale factors.

While the first step in the optimization sequence gave rise to an energy lowering of only 0.3 kcal/mole the overall stabilization of the *cis* form brought about by rescaling amounted to 1.8 kcal/mole. As this energy lowering was more than expected, a similar investigation for the skew and *trans* form became necessary. In Table VII optimum ξ -values obtained by the rescaling procedure for the three H₂O₂ conformations are compared with the standard values of Ref. 8. Table VIII

summarizes energies, barrier values and structural parameters evaluated with the [4s3p1d/2s1p] basis⁸ and its rescaled versions.

The calculated figures indicate energy gains of the same magnitude, namely 1.8 (*trans*) and 1.5 kcal/mole (skew). A slight lowering of 0.2 kcal/mole for the *cis* barrier is paralleled by a similar reduction of the *trans* barrier. Thus, the overall agreement with experiment has deteriorated.

It is interesting to note that the changes in the basis do not occur for the d functions but for the outer oxygen s functions which become more diffuse and the hydrogen s set which contracts relatively to the DW basis. These tendencies are valid for all conformations though somewhat more pronounced in the planar forms. In addition, a significant expansion of the hydrogen 2p functions marks the *cis* form. The latter is not surprising in view of their special significance for charge redistribution. The more the 2p functions expand the better is their overlap with the diffuse O functions and, hence, the location of charge in the OH bond region rather than the area of the O atoms. In accordance with this is the enlargement of the 2p(H) gross populations in the *cis* form (0.0716 compared to 0.0457 in the *trans* form).

Despite the considerable changes of ξ -values only a moderate stabilization of the *cis* form results. By inspection of the second derivatives $\partial^2 E / \partial \xi^2$ it appears that the curvature of the energy hypersurface calculated in the space of the basis set is very low for the 2p(H) GTF's and only moderate for s(H) GTF's. Large changes of these functions and, thereby, large changes in the wavefunction produce only slight lowerings in the energy.

We have also attempted to improve the theoretical *cis* barrier by employing a larger, more flexible basis set. For this purpose van Duijneveldt's (11s6p2d/6s2p) uncontracted basis³⁰ seemed appropriate. The total energies obtained with it (Table VIII, column 3) are closer

TABLE VII. Optimum scale factors of the [4s3p1d/2s1p] basis calculated for *cis*, skew, and *trans* H₂O₂ at the HF level.

Basis function	<i>cis</i>	skew	<i>trans</i>	<i>trans</i> Ref. 8
s (O)	1.0	1.0	1.0	1.0
s' (O)	1.001	1.001	1.001	1.0
s'' (O)	0.824	0.832	0.816	1.0
s'''(O)	0.862	0.880	0.837	1.0
p (O)	1.018	1.018	1.017	1.0
p' (O)	1.013	1.015	1.012	1.0
p'' (O)	0.995	1.001	1.002	1.0
d (O) ^a	1.023	0.995	1.014	1.0
s (H)	1.371	1.319	1.324	1.275
s' (H)	1.432	1.405	1.403	1.275
p (H) ^b	0.803	0.981	1.008	1.0

^aValues of the Gaussian d exponent are: 0.91 (Ref. 8), 0.935 (*trans*), 0.901 (skew), 0.953 (*cis*).

^bValues of the Gaussian p exponent are: 0.88 (Ref. 8), 0.895 (*trans*), 0.846 (skew), 0.567 (*cis*).

TABLE VIII. Energies and geometrical parameters obtained with the $[4s3p1d/2s1p]$ and the $(11s6p2d/6s2p)$ basis at the Hartree-Fock level.

Conformation	Parameter	$[4s3p1d/2s1p]$ Ref. 8	$[4s3p1d/2s1p]$ Optimum scale factors	$(11s6p2d/6s2p)$
Absolute energies (hartree)				
skew		-150.82191	-150.82424	-150.84548
trans		-150.82016	-150.82304	-150.84318
cis		-150.80860	-150.81142	-150.83323
Barrier heights V (kcal/mole)				
trans		1.10	0.75	1.44
cis		8.35	8.04	7.69
Structural parameters ^a				
skew	$R(\text{OH})$	0.946	0.945	0.943
	$R(\text{OO})$	1.393	1.390	1.390
	$\alpha(\text{OOH})$	102.5	102.8	102.9
	$\theta(\text{HOOH})$	113.7	114.9	111.2
trans	$R(\text{OH})$	0.946	0.946	0.942
	$R(\text{OO})$	1.401	1.401	1.398
	$\alpha(\text{OOH})$	101.1	101.3	101.2
cis	$R(\text{OH})$	0.946	0.946	0.943
	$R(\text{OO})$	1.399	1.398	1.398
	$\alpha(\text{OOH})$	107.1	106.8	106.9

^aBond lengths in Å, angles in degrees.

to the estimated HF limit of -150.93 hartree⁶ than any other RHF value so far reported. Accordingly, the computed *cis* barrier (7.7 kcal/mole) confirms the expected lowering due to increased basis set flexibility. Not expected was the rise of the *trans* barrier to 1.4 kcal/mole. An analysis of the gross atomic populations, however, indicates that exponent optimization may decrease the barriers in a similar way as found for the DW basis. Hence, barrier heights of 7.4 (*cis*) and 1.1 (*trans*) kcal/mole seem reasonable for the optimum $(11s6p2d/6s2p)$ basis.

In the following, correlation effects which we have already confirmed with regard to equilibrium geometries are reexamined with the $[4s3p1d/2s1p]$ basis. The results of second order RS-MP perturbation calculations are depicted in the first column of Table X. Compared to the energies obtained with basis D (see Tables IV and VI) a lowering of 0.11 hartree is gained with the DW basis. Almost two thirds of this difference result from an increase of the correlation energy, thus reflecting an enhanced sensitivity of correlation effects with respect to basis set improvements. Less significant are the relative changes in energy: There is an overall improvement in the computed barrier values, but this is solely achieved at the HF-level (see Tables I and VIII) while the decrease of the *trans* barrier and the increase of the *cis* barrier characteristic for correlation corrected energies has remained. If these effects are separated into a direct one which shows up in the relative second order correlation energies and an indirect one which enters already at the HF level on grounds of correlation dependent bond lengthening, then the former

is responsible for the reduction of the *trans* barrier (-0.4 kcal/mole; see Table X) while the latter increases the *cis* barrier (0.2 kcal/mole; see Tables VIII and X). Nevertheless, both contributions to the two barrier values continue to decrease with an improvement of the basis. For example, the differences $V_{trans}(\text{RS-MP}) - V_{trans}(\text{RHF})$ obtained with basis sets C, D, and the DW basis tend to zero (-0.34 , -0.27 , -0.23 kcal/mole) as do the corresponding differences for the *cis* barrier (0.28, 0.19, 0.15 kcal/mole).

We have pursued the question of correlation effects one step further by investigating rescaled versions of the $[4s3p1d/2s1p]$ basis at the RS-MP level. All RS-MP calculations discussed so far in this paper were performed under the assumption that basis sets chosen to minimize HF energies also provide reasonable second order correlation energies. Judging from the results of Tables IV and VI such an approximation seems to be correct for uniformly scaled basis sets. However, for individually scaled basis sets this cannot be confirmed, as can be seen from the data of Table X, where, in the second column, total and relative energies obtained with the optimum scale factors of Table VII are listed. Although a further decrease of total energies by ~ 0.004 hartree has occurred, relative changes indicate a strong deterioration of results. Despite a 1 kcal/mole stabilization at the HF level the minimum of the skewed form is totally lost by an unfavorable second order correlation energy. Obviously, a consistent description of the three H_2O_2 conformations is not possible with optimum HF scale factors at the RS-MP level.

TABLE IX. Optimum scale factors of the $[4s3p1d/2s1p]$ basis calculated for *cis*, skew, and *trans* H_2O_2 at the level of second order RS-MP perturbation theory.

Basis function	<i>cis</i>	skew	<i>trans</i>
<i>s</i> (O)	1.0	1.0	1.0
<i>s'</i> (O)	1.001	1.001	1.001
<i>s''</i> (O)	0.889	0.890	0.890
<i>s'''</i> (O)	0.886	0.882	0.878
<i>p</i> (O)	1.033	1.032	1.033
<i>p'</i> (O)	1.036	1.036	1.036
<i>p''</i> (O)	0.997	1.000	1.001
<i>d</i> (O) ^a	1.123	1.128	1.125
<i>s</i> (H)	1.378	1.339	1.342
<i>s'</i> (H)	1.458	1.445	1.448
<i>p</i> (H) ^b	0.769	0.882	0.835

^aValues of the Gaussian *d* exponent are: 1.148 (*cis*), 1.158 (skew), 1.151 (*trans*).

^bValues of the Gaussian *p* exponent are: 0.520 (*cis*), 0.595 (skew), 0.613 (*trans*).

Before this failure is analyzed in detail we present the results of rescaling performed at the RS-MP level. The same sequence of optimizations described above yielded the optimum RS-MP ζ -values of Table IX. The corresponding energies and structural parameters are summarized in the third column of Table X. Comparing the first and the third column of Table X, significant improvements of absolute and relative energies can be observed. The energy lowering due to rescaling of basis functions exceeds with 7–8 kcal/mole more than four times the corresponding energy gain achieved at the HF level. About 75% of the estimated H_2O_2 correlation energy of 0.61 hartree⁶ is now covered. In contrast to the data of column 2 there is consistency in the relative energy changes. If more importance is attached to the spectroscopical *trans* barrier,^{9–12} then, the RS-MP barriers obtained with optimum RS-MP scale factors are in better agreement with experiment than (1) the corresponding HF-values (Table VIII), (2) the RS-MP values of the smaller basis sets C and D (Table IV), and (3) the RS-MP values of the original DW basis set (first column of Table X). Nevertheless, the significance of the cor-

TABLE X. Summary of total energies, second order correlation energies, barrier values, and structural parameters obtained with the $[4s3p1d/2s1p]$ basis and its rescaled versions at the level of RS-MP perturbation theory.

Conformation	Parameter	Scaling as in Ref. 8	Rescaled at the HF-level	Rescaled at the RS-MP level
Absolute energies (hartree)				
skew		-151.26844	-151.27256	-151.28031
<i>trans</i>		-151.26704	-151.27226	-151.27882
<i>cis</i>		-151.25289	-151.26254	-151.26736
Second order correlation energies (hartree)				
skew		-0.45055	-0.45183	-0.46213
<i>trans</i>		-0.45117	-0.45427	-0.46250
<i>cis</i>		-0.45052	-0.45476	-0.46226
Barrier heights <i>V</i> (kcal/mole)				
<i>trans</i>		0.87	-0.50	0.94
<i>cis</i>		8.50	6.29	8.13
Relative contributions of correlation energies to barriers (kcal/mole)				
<i>trans</i>	total	-0.39	-1.53	-0.23
	intra	-1.27		-1.73
	inter	0.88		1.49
<i>cis</i>	total	0.02	-1.83	-0.08
	intra	-2.83		-3.16
	inter	2.85		3.07
Structural parameters (distances in Å, angles in degrees)				
skew	<i>R</i> (OH)	0.970	no	0.967
	<i>R</i> (OO)	1.456	optimization	1.451
	α (OOH)	99.5	performed	99.3
	Θ (HOOH)	118.8		119.3
<i>trans</i>	<i>R</i> (OH)	0.969		0.966
	<i>R</i> (OO)	1.468		1.464
	α (OOH)	98.0		97.7
<i>cis</i>	<i>R</i> (OH)	0.970		0.967
	<i>R</i> (OO)	1.466		1.460
	α (OOH)	104.3		103.6

relation dependent improvements in the barriers is limited: there is nearly complete cancellation of intra- and interpair effects which leads to relative second order contributions to the barriers in the order of 0.2 and 0.1 kcal/mole. Of somewhat larger magnitude are the indirect effects caused by correlation dependent changes in the geometry. But again, cancellation due to opposite signs of direct and indirect contributions lowers the overall effect. If possible contributions of higher order especially due to three and four body correlations are neglected, it is safe to say that correlation effects play no major role in the determination of the barrier values of H_2O_2 .

In this respect, RS-MP results obtained with optimum HF scale factors are misleading. As can be seen from Tables VII and IX basis functions tend to contract at the RS-MP level. For the s and p sets this tendency is superimposed by the size behavior found at the HF level. Hence, the oxygen outer s functions become less diffuse while the hydrogen s functions become more strongly contracted. The changes of ζ -values computed for the polarization functions are different. The d set almost uniformly tightens at all rotational angles which stands in marked contrast to the small and varying changes of $\zeta_{3d}(\text{HF})$. The $2p$ GTF's of the H set, on the other hand, become significantly more diffuse, thus opposing the contraction tendency of the other basis functions. At the HF level a low $2p$ scale factor is also found for the *cis* form but not for the two other forms. In this respect, differences between the three ζ -sets of Table IX are smaller than at the HF level. The sensitivity of basis functions with regard to internal rotation has diminished which is in line with the small correlation contributions to the relative energies.

If the total gain in correlation energies is attributed to the various changes of scale factors the tightening of the d functions combined with the expansion of the $p(\text{H})$ functions accounts for 4 kcal/mole, i. e., more than 50% of the total energy decrease and twelve times as much as the corresponding value at the HF level. The increased importance of optimum scaled polarization functions is also documented by second derivatives. The RS-MP energy surface in ζ_{3d} space is much steeper than the corresponding HF surface. Curvature has also increased with respect to $s'''(\text{O})$, $s(\text{H})$, $s'(\text{H})$ and $p(\text{H})$ scale factors, the latter increase being of the order of 100% compared to HF values.

On the basis of these results the failure of a description with optimum HF basis functions can be explained. The $\zeta(\text{HF})$ -values (Table VII) indicate relatively large distortions of the wavefunction during the rotational process which is not the case at the RS-MP level. An artificially exaggerated dependence of scale factors, therefore, leads to erroneous results while uniformly scaled basis sets (C, D and DW) conserve the rotational independence of correlation energies and, hence, the dominance of energy differences resulting at the HF level. We have supported this conclusion by two additional calculations. First, we have repeated RS-MP calculations for the *cis* and *trans* form using the optimum HF scale factors of the skew form and the struc-

tural parameters listed in column 1 of Table X. The barrier values thus obtained (0.83 and 8.64 kcal/mole) are in satisfactory agreement with results of the unscaled $[4s3p1d/2s1p]$ basis. Similar improvements result when scale factors of the skew form are adjusted to optimum ζ -values of the *trans* form. It is interesting to note that a single change of ζ_{3d}^{C} from 0.900 to 0.935 (ζ_{3d}^{C} of the *trans* form; see Table VII) lowers the second order correlation energy by 1.1 kcal/mole and raises the *trans* barrier to 0.7 kcal/mole, thus reflecting the necessity of rescaled $3d$ functions at the RS-MP level.

It remains to analyze the general contraction tendency of the optimum RS-MP basis set. This can be understood as a result of correlated electron movements. An enlarging of the molecular dimensions, especially the length of the OO distance, facilitates attempts by the electrons to avoid each other. Similarly, a redistribution of charge from inner atomic regions to the outer sphere of an atom improves electron correlation. The increase of repulsive forces caused by outer-sphere charges at the two O atoms which we found to be characteristic for the HF wavefunctions should now be less pronounced. As was noted above an expansion of the $s''(\text{O})$ functions leads to an accumulation of charge in the (inner) s'' region. If this expansion is reduced charge is redistributed to the (outer) s''' region. In the same way, the tightening of the oxygen $2p$ and the hydrogen $1s$ sets is connected with a shift of charge to the outer functions. The calculated RHF gross atomic populations support our conclusion, although final proof should be provided by the first order corrections of the wavefunctions which we have not calculated.

It should be noted that the tightening of the d functions resembles the size behavior of polarization functions used for the *ab initio* description of positively charged species: Compared to the neutral molecules an increase of ζ_{3d}^{C} by 0.35 was found in exponent optimizations.⁵³ As the redistribution of charge at the oxygen atoms certainly leads to a descreening of the $3d$ GTF's their size contraction can also be seen as a result of electron correlation.

VII. DISCUSSION OF EXPERIMENTAL VALUES

Structural and conformational investigations of gaseous hydrogen peroxide or its deuterated analogue have been undertaken by means of electron diffraction⁵⁴ as well as infrared and MW spectroscopy.⁹⁻¹² In addition, crystalline H_2O_2 and D_2O_2 have been studied by x-ray⁵⁵ and neutron diffraction technique.⁵⁶⁻⁵⁸ Despite the wealth of collected spectroscopic data there exists a surprising controversy with regard to proposed structural and conformational parameters. Based on experimental arguments, criticism has been raised with regard to published barrier values by Ewig and Harris,⁵⁹ and with regard to published geometries by Busing and Levy,⁵⁶ by Khachkuruzov and Przhivalskii,⁶⁰ and by Giguère and Srinivasan.⁶¹ Unfortunately, theoretical studies have shown a tendency to support another set of experimental parameters with any refinement of calculation, thus rather complicating than clarifying the situation. Therefore, a discussion of experimental parameters in con-

TABLE XI. Experimental geometry of hydrogen peroxide and deuterium peroxide as determined by various spectroscopic methods.^a

Authors	Redington, Olson, Cross 1962 Ref. 9	Redington, Olson, Cross this work	Busing, Levy 1965 Ref. 56	Prince, <i>et al.</i> 1975 Ref. 57	Giguère, Srinivasan 1977 Ref. 61	Khachkuruzov, Przhevalskii 1974 Ref. 60
Method	ir	ir ^c	Neutron	Neutron	ED ^e	IR, MW ^f
	r_0 -values	r_0 -values	Diffraction	Diffraction ^d		r_e -values
$R(\text{OH})$	0.950(5) ^b	0.967(5) ^b	0.988(5)	0.993(2)	0.965(5) ^b	0.965(5) ^b
$R(\text{OO})$	1.475(4)	1.463(4)	1.453(7)	1.455(2)	1.467(5)	1.452(4)
$\alpha(\text{OOH})$	94.8(2.0)	99.3(2.0)	102.7(3)	102.1(1.0)	98.5(1.0)	100(1.0)
$\theta(\text{HOOH})$	119.8(3.0)	120.2(3.0)	90.2(6)	90.8(5.0)	120.(2)	119.1(1.8)

^aBond distances in Å, bond angles in degree. Experimental uncertainties given in parenthesis.

^bAssumed values.

^cReinterpretation of infrared data of Ref. 9 using the theoretical OH bond length of Table X.

^dNeutron diffraction of D₂O₂.

^eOO bond length taken from Ref. 54.

^fReinterpretation of the spectroscopic data of Refs. 9, 10, and 12.

nection with the *ab initio* values of the preceding section is desirable.

Structural parameters (Table XI). The first complete set of geometrical data of H₂O₂ was proposed by Redington, Olson, and Cross⁹ on the basis of the rotational constants of the ground vibrational state. This set was later used in two independent spectroscopic studies^{10,12} in order to compute the inertial parameters of H₂O₂. The resulting agreement between calculated and observed rotational transitions led the authors to the conclusion that their measurements confirmed the bond lengths and the OOH bond angle suggested in Ref. 9. Busing and Levy⁵⁶ were the first to criticize the values of Ref. 9 by pointing out the specific dilemma of structural determination of H₂O₂ from rotational constants. There are only three moments of inertia but four internal coordinates in skewed H₂O₂. Hence, only the functional dependence of three parameters on the fourth can be gained from vibrational-rotational constants. Definite values are possible, if one parameter is fixed in a more or less plausible way. The final set of parameters proposed in Ref. 9, for example, was obtained by setting the OH distance to 0.950 Å. This choice was based on an argument given by Bent⁶² who anticipated that a replacement of one H atom in H₂O by a more electronegative atom should shorten the remaining OH bond due to increased s character. That this assumption cannot be held either on experimental or theoretical grounds is easily shown: (1) The similarity of OH and OD bond data obtained by neutron diffraction of H₂O₂,⁵⁶ D₂O₂,⁵⁷ and D₂O⁶³ does not comply with the assumed shortening (argument given first by Busing and Levy⁵⁶). (2) The $R(\text{OH})$ value found for HOF ($R(\text{OH}) = 0.964$ Å, Ref. 64) is clearly longer than in H₂O ($R(\text{OH}) = 0.957$ Å, Ref. 19) (argument given first by Khachkuruzov *et al.*⁶⁰). (3) At all calculational levels performed in this work the $R_e(\text{OH})$ value of H₂O turned out to be shorter by ~0.01 Å.⁶⁵

The consequences of an erroneous choice of $R(\text{OH})$

become evident when columns 1 and 2 of Table XI are compared. Due to a longer OH bond assumed for the second set the OO bond length is reduced by 0.01 Å and the OOH angle increased by more than 4° while the dihedral angle has hardly changed.⁶⁶ We have taken for $R(\text{OH})$ the RS-MP value of Table X which is an equilibrium value, while the spectroscopic parameters are defining the r_0 -structure of H₂O₂. Observed OH bond lengths,^{19,20} however, indicate that $R_0(\text{OH})$ and the theoretical $R_e(\text{OH})$ are comparable within an uncertainty of 0.005 Å. Hence, column 2 provides a reasonable set of r_0 -parameters which prove the OO distance and the OOH angle of Ref. 9 to be highly misleading. In this connection it is interesting to note that the fruitless attempts of theoreticians to compute an OOH angle significantly lower than 100° was based on the validity of the data of Ref. 9.

In order to make a direct comparison between experiment and theory a set of experimentally based equilibrium parameters is necessary. Such a set has been evaluated by Khachkuruzov *et al.*⁶⁰ from the effective rotational constants of Ref. 9. As can be seen from Table XI their r_e -parameters are in excellent agreement with our best values depicted in the last column of Table X. Nevertheless, a critical examination of this agreement is necessary, especially in view of the recent arguments given by Giguère and Srinivasan.⁶¹

These authors expect an OO distance of 1.467 Å rather than 1.452 Å while their proposed angle values, though somewhat different from those of Ref. 60, are still in good agreement with our theoretical values. Their predictions are directly based on an ED measurement of $R(\text{OO})$,⁵⁴ indirectly on the OO stretching frequency in the vapor and the solid⁶⁷ as well as neutron diffraction results of Ref. 56 and 57 as discussed by Pedersen.⁵⁸ Although these arguments may have significance with regard to thermal average values of the OO distance, they do not allow any conclusion to be reached with re-

TABLE XII. Experimental barrier values (kcal/mole) and dihedral angles (degrees) of H_2O_2 and D_2O_2 as determined by far ir and MW spectroscopy.

Authors	Redington Olson, Cross 1962 Ref. 9	Hunt, <i>et al.</i> 1965 Ref. 10	Hunt, Leacock 1966 Ref. 11	Oelfke, Gordy 1969 Ref. 12	Ewig, Harris 1969 Ref. 59	
Molecule	H_2O_2^a	H_2O_2^a	D_2O_2^a	H_2O_2^a	H_2O_2^c	D_2O_2^c
V_{trans}	0.85	1.10	1.08	1.1	1.10	1.08
V_{cis}	3.71	7.03	7.06	7.0	7.57	8.80
Θ	109.5	111.5	110.8	120 ^b	112.8	115.3

^aBased on the structural data of the infrared analysis of Redington, Olson, and Cross, Ref. 9.

^bTaken from the lower level of the ground state doublet.

^cReinterpretation of the data of Refs. 10 and 11 by a method which needs no *a priori* knowledge of the molecular structure.

gard to the true $R_e(\text{OO})$ length unless all corrections are known.⁶⁸ More serious is the indication of Giguère *et al.* that the rotational constants of the Russian authors⁶⁹ do not comply with experimental constants and, consequently, their equilibrium structure has to be rejected. In order to check on this argument we have repeated the calculation of $R_e(\text{OO})$ from moments of inertia using the values presented by Giguère *et al.*⁶¹ The equilibrium value of 1.453 Å obtained in this way is in clear contrast with an OO distance of 1.467 Å but in full accordance with the value of Ref. 60 and our theoretical result of 1.451 Å (Table X). It seems, therefore, appropriate to support the geometrical parameters of Ref. 60 as valid equilibrium data, while the corrected values of Ref. 9 (2nd column of Table XI) provide a reasonable r_0 -structure.

Barrier values (Table XII). As can be seen from tabulated barrier heights there exists no ambiguity with regard to the *trans* barrier. A value of 1.1 kcal/mole has been widely accepted. Although three of the published *cis* barriers suggest a similar accuracy of this value, some doubts still exist. In Table XII it is indicated that all spectroscopic measurements are based on the erroneous structural parameters of Ref. 9. Ewig and Harris⁵⁹ who determined the barrier values directly from the torsional frequencies of Ref. 10 without any explicit usage of geometrical data found that the *cis* value is affected by an erroneous geometry while the *trans* barrier is not. These authors further demonstrated that "the experimental data are all very insensitive to the *cis* barrier height."⁵⁹ Small changes in the observed torsional frequencies raised the barrier value from 7.6 to 14.4 kcal/mole, while the *trans* barrier and the shape of the torsional potential between 140° and 220° remained unchanged. Dunning and Winter,⁸ therefore, concluded that quantum chemistry provides a better account of the *cis* barrier height than experiment can do at present. A value close to 7.4 kcal/mole obtained in this work must be considered as a reasonable estimate of the *cis* barrier height.

It is interesting to note that Ewig and Harris found not only larger *cis* barriers for H_2O_2 and D_2O_2 but also larger dihedral angles than those obtained by Hunt *et*

al.^{10,11} A low *cis* barrier based on the structure of Ref. 9 and a low dihedral angle seem to be interrelated. The very accurate measurement of Θ_0 from the Fourier expansion of the inertial parameter $\gamma(\Theta)$ published by Oelfke and Gordy¹² certainly gives the most reliable clue to an equilibrium dihedral angle close to 120°. While correlation corrected theory is in line with this value RHF calculations predict a ten degree smaller angle. In this respect, the Θ_e -values close to 120° which are obtained with smaller augmented basis sets (see Table II, and Ref. 1) are fortuitous. They result from slight overestimations of the OH bond polarity which forces the H_2O_2 angles to widen. Our value of 111° calculated with a (11s6p2d/6s2p) basis provides a reasonable estimate of the HF dihedral angle. If theory includes correlation effects, the angle is widened because of better electron correlation in the *trans* form. We conclude that only *ab initio* calculations which go beyond the single determinant ansatz are capable of providing the true equilibrium dihedral angle.

VIII. CONCLUSION

Calculations presented here are the most accurate so far performed for H_2O_2 . They allow for (1) flexibility of the basis by including two or more sets of polarization functions, (2) rescaling of basis functions at all rotational angles, (3) correction for correlation errors and (4) complete structure optimization. We find that at the HF level of theory an accurate recording of barriers to internal rotation is possible if (1), (2), and (4) are observed. Noteworthy, is the importance of 2p polarization functions at hydrogen for the description of the *cis* form. Inclusion of these functions reduces the OH bond polarity and, thereby, the height of the *cis* barrier. Similarly, improvements in the s, p basis work out, i. e., the height of a computed *cis* barrier unmistakably reveals deficiencies in the basis set. In this respect, the seemingly good equilibrium structures obtained with small basis sets are fortuitous. They result from an overestimation of charge separation documented by the computed high *cis* barrier and high dipole moment. Near HF calculations, however, suggest barriers close to 1.1 (*trans*) and 7.4 (*cis*) kcal/mole. They also lead to a short OO bond length of 1.39 Å and, accordingly, predict an erroneous equilibrium structure with a minimum dihedral angle of about 111°. This failure of the HF method is easily rationalized in terms of charge concentration and separation. If the basis set is flexible enough to hold charge close to the oxygen nuclei which seems to be possible in an independent electron model, repulsion of the O atoms is low and widely compensated by overlap. Hence, a short OO length results. Arguments that basis set improvements due either to augmentation with bond functions¹⁴ or to explicit scaling of polarization functions,⁵ will lead to a better description of structural parameters, have to be rejected. Only, if theory allows for electron correlation, can accurate equilibrium structures be obtained. Correlation corrected parameters indicate excellent agreement between theory and experiment. In addition, they allow the proposed r_0 -structure of H_2O_2 ⁹ to be improved and experimental parameters so far proposed to be consid-

ered. The potential minimum calculated at $\Theta = 119^\circ$ (RS-MP value) can be explained by simple MO theory. However, the more traditional approach in terms of OH bond and lone-pair staggering is clearly misleading.

Although there are large contributions of inter- and intrapair correlation energies to the barrier values, their net effect is rather small due to extensive cancellation. Correlation dependent contributions are further diminished by indirect effects resulting from changes in equilibrium geometries. Contrary to arguments given previously¹³ we find that correlation plays no major role in the determination of the *cis* or *trans* barrier of H₂O₂. If, however, a basis set is used which is not properly scaled erroneous barrier values are calculated at the RS-MP level. In so far our study stresses the importance of exponent optimization especially for the polarization functions. The tendency of basis functions to contract at the RS-MP level and to become less dependent on the dihedral angle indicates a decrease of charge concentration due to correlated electron movements.

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