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Polarization Functions and Geometry Optimization in *ab initio* Calculations of the Rotational Barrier in Hydrogen Peroxide

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Ab initio calculations have been carried out for the hydrogen peroxide molecule with different-size Gaussian basis sets in an attempt to determine the relative importance of carefully refined geometry and improvement of the wave function for calculation of the trans rotational barrier. *d*-type polarization functions on the oxygen atoms are found to be essential for calculation of a trans rotational barrier. Using the (O/7,3,1) (H/4,1) basis set, a trans rotational barrier of 0.63 kcal/mole is calculated (exp. value, 1.1 kcal/mole). Except for refined calculations approaching the Hartree-Fock limit, careful geometry optimization is found to be of secondary importance to the inclusion of *d*-type functions on the oxygen atoms and may be carried out satisfactorily using a smaller basis set than is used for the energy calculations. The (O/7,3) (H/4,1) basis set which includes *p*-type polarization functions on the hydrogen atoms yields geometrical parameters in good agreement with experiment as well as good charge distribution between the hydrogen and oxygen atoms.

Ab-initio Rechnungen für das Wasserstoffperoxidmolekül wurden mit Basissätzen verschiedener Größe durchgeführt um den Einfluß einer genauen Geometrie und einer Verbesserung der Wellenfunktion auf die Berechnung der *trans*-Rotationsbarriere zu untersuchen. Es zeigte sich, daß *d*-Polarisationsfunktionen für solche Rechnungen äußerst wichtig sind. Mit dem Basissatz (O/7,3,1) (H/4,1) wurde die Rotationsbarriere mit 0,63 kcal/Mol berechnet (exp.: 1.1 kcal/Mol). Außer bei Rechnungen nahe am Hartree-Fock-Limit zeigte sich, daß die Geometrieoptimisierung gegenüber der Mitnahme von *d*-Funktionen von sekundärer Bedeutung ist und daher mit einem kleineren Basissatz durchgeführt werden kann, als die Energieberechnung. Der (O/7,3) (H/4,1) Basissatz, der *p*-Funktionen am Wasserstoffatom einschließt gibt die Geometrie und die Ladungsverteilung zwischen Wasserstoff- und Sauerstoffatom in guter Übereinstimmung mit dem Experiment.

Introduction

In an attempt to explain barriers to internal rotation, a number of semi-empirical and *ab initio* calculations have been performed using hydrogen peroxide as the simplest molecule having a barrier to internal rotation [1–6]. Although these attempts have quite generally predicted the trans conformation to be more stable than the cis conformation, most have failed to predict the experimental potential energy minimum at a dihedral angle of about 120° and show only a monotonic decrease in energy as the dihedral angle is increased from 0° to 180° with the trans-planar conformation being the most stable. Veillard [6] has carried out *ab initio* LCAO–MO–SCF calculations for the H_2O_2 molecule using

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a large basis set of Gaussian-type functions including *d*-type functions for O and *p*-type functions for H, and has obtained energies approaching the Hartree-Fock limit. Further, he has minimized the energy with respect to variations in bond lengths and bond angles at each rotational angle calculated. These efforts have yielded a trans rotational barrier of 0.6 kcal/mole (experimental value, 1.1 kcal/mole) with a potential energy minimum at a dihedral angle of 123°. The rotation from 0° to 180° is also accompanied by a decrease of 0.025 Å in the O–O bond length and a decrease of 5.4° in the OOH bond angle. (The O–H bond length was not optimized.) From these results, Veillard has concluded that improvement of the wave function by using larger basis sets which include polarization functions and optimization of bond lengths and bond angles are equally important in achieving rotational barriers which approach the Hartree-Fock limit and he further states a belief that these two requirements must be satisfied simultaneously.

An examination of Veillard's results shows clearly that the use of geometries which are in error by as much as 0.025 Å in O–O bond length and 5.4° in bond angle (such as would result from using the same bond lengths and bond angles for the cis- and trans-conformations of H_2O_2) would yield calculated energies on the order of 1.8 kcal/mole greater than the minimum energy calculated at the optimum geometry, an amount that is more than half again as large as the trans rotational barriers and that, indeed, refined calculations without geometry optimization would not be satisfactory.

It is not apparent from Veillard's results, however, what degree of expansion of basis sets is necessary to calculate satisfactory energy differences between two rotational conformations (as opposed to total energy of a single conformation) when the bond lengths and bond angles are optimized for each conformation; nor is it apparent whether a smaller basis set may be used for optimization of geometry prior to performing a single, good energy calculation with a larger basis set. (Forsén and Roos [7] have followed this procedure, but without particular justification, in their studies of the protonation of the carbon monoxide and the nitrogen molecule.) It is important to consider these possibilities which might allow geometry optimization, and perhaps energy calculations as well, with basis sets smaller than required to obtain total energies approaching the Hartree-Fock limit for the following reasons. (1) The number of two-electron integrals to be evaluated in an *ab initio* calculation increases roughly as the fourth power of the number of functions in the basis set. (2) In the IBMOL programs, evaluation of a two-electron integral involving one or more *d*-type functions requires approximately 4–8 times as long as evaluation of a two-electron integral involving only *s*- and *p*-type functions (only approximately 3 times as long if Roos's multiplication table [20] is used) and, thus, computation time may increase even more rapidly than the fourth power of the number of basis functions when the basis functions being added are *d*-type. (3) The number of points to be calculated in mapping a multi-dimensional energy surface sufficient to locate a local minimum increases rapidly with the size and complexity of the molecule. (Even with the small molecule H_2O_2 and assuming the two O–H bond lengths as well as the two OOH bond angles to be equal to each other, there are three coordinates to be varied at each torsional angle; a systematic search in three dimensions will require the calculation of at least ten points and more will be required if the initial values chosen are very far from the optimum values.) It is to these considerations and questions that this study is directed.

Calculations

The H_2O_2 molecule was used as a test case because (a) it is a small enough molecule that calculations using reasonably large basis sets are not prohibitive, (b) the trans rotational barriers is small and its successful prediction provides a fairly sensitive test of the method, and (c) Veillard's results [6] using a large basis set with calculated energies near the Hartree-Fock limit are available for comparison. Calculations were carried out at dihedral angles of 120° and 180° only.

The calculations are of the LCAO–MO–SCF type using basis sets of contracted Gaussian-type functions. The smallest basis set used was made up of five *s*-type and two *p*-type Gaussian functions for the oxygen atoms (O/5,2) and two *s*-type functions for the hydrogen atoms (H/2). This basis set will also be designated (5,2/2). This set was suggested by Sachs, Geller and Kaufman [8] as being the smallest basis set with which molecular geometries could be calculated with any degree of reliability. This basis set was contracted to two *s*-type and one *p*-type function for the oxygen atoms $\langle O/2,1 \rangle$ and one *s*-type function for the hydrogen atoms $\langle H/1 \rangle$. Contracted basis sets will be designated by brackets and, thus, this contracted basis set is designated $\langle 2,1/1 \rangle$. In studies of CF_2 with this basis set (uncontracted), Sachs *et al.* [8] calculated an equilibrium C–F bond length that is 2.4% longer than the experimental value and a FCF bond angle 1.0° larger than the experimental value. We are interested, however, in calculating bond lengths and bond angles that compare favorably, not so much with experimental values as with the optimum values calculated using a large basis set. If the comparison is no better than with the experimental values, it is probable that nothing can be gained by use of this small basis set, but if some of the systematic error introduced by using the small basis set also exists in calculations using the larger basis set, it may be possible to use the optimum geometrical parameters obtained with this small basis set for more refined calculations.

An intermediate-size basis set was constructed of seven *s*-type and three *p*-type functions for the oxygen atoms and four *s*-type functions for the hydrogen atoms (7,3/4); this set was contracted to $\langle 4,2/2 \rangle$. This set may be considered comparable to a Pople STO 2*G* set [9] which has been shown by Baird [10] to yield bond lengths generally within 0.01 Å of the experimental value for several diatomic and simple polyatomic molecules.

Roos and Siegbahn [11] have shown the necessity of adding polarization functions (*d*-type functions for O and *p*-type functions for H) before further increasing the (*s*, *p*/*s*) basis set. Accordingly, the third basis set used was (7,3,1/4,1) contracted to $\langle 4,2,1/2,1 \rangle$.

Finally, as results began to emerge, it became apparent that the *p*-type functions on hydrogen were, in many respects, more important than the *d*-type functions on oxygen. Since inclusion of *p*-type functions on hydrogen constitutes only a

Table 1. Gaussian basis functions used for hydrogen peroxide calculations

Atom	Basis set	Source	Type	Exponent	Expansion coefficients			Contraction coefficients
					1*s*	2*s*	2*p*	
H	(H/2)→⟨H/1⟩	Huzinaga [12]	*s*	1.66560[a]	0.27441			0.27441
				0.251909	0.82123			0.82123
	(H/4)→⟨H/2⟩	Huzinaga [12]	*s*	16.7019[a]	0.01906			0.01906
				2.51663	0.13424			0.13424
				0.567196	0.47449			0.47449
				0.154146	0.50907			0.50907
O	(O/5,2)→⟨O/2,1⟩	Whitman and Hornback [13]	*s*	736.6	0.0217	−0.0050		0.0217
				112.9	0.1447	−0.0316		0.1447
				26.04	0.4604	−0.1380		0.4604
				7.212	0.5061	−0.1698		0.5061
				0.5764	0.0215	1.0436		1.0436
			p	3.188			0.3503	0.3503
				0.5486			0.8005	0.8005
	(O/7,3)→⟨O/4,2⟩	Roos and Siegbahn [14]	*s*	2714.89	0.004324	−0.000975		0.004324
				415.725	0.032265	−0.007518		0.032265
				91.9805	0.156410	−0.037030		0.156410
				24.4515	0.447813	−0.130541		0.447813
				7.22296	0.481602	−0.204753		0.481602
				1.06314	0.042157	0.504708		0.504708
				0.322679	−0.011360	0.616743		0.616743
			p	7.75579			0.129373	0.129373
				1.62336			0.481269	0.481269
				0.365030			0.604484	0.604484

[a] Huzinaga's exponents for H atom multiplied by Wahlgren's scale factor of 1.25 as cited in Roos and Siegbahn [11].

slight expansion of the (7,3/4) basis set, a final set of calculations was carried out using a (7,3/4,1) basis set contracted to ⟨4,2/2,1⟩. For simplicity of discussion, henceforth, all these basis sets will be referred to with the uncontracted notation and the appropriate contractions will be understood.

The orbital exponents and expansion coefficients for different atoms and different-size Gaussian basis sets were taken from several sources and are listed, together with their sources, in Table 1. The common practice of using atomic expansion coefficients as contraction coefficients for molecular calculations has been discussed by Salez and Veillard [15] and that procedure has been followed in this work. The grouping of basis functions to form contracted functions was carried out observing Dunning's rules [16] and the groupings as well as the unnormalized contraction coefficients used are given in Table 1. The orbital exponents used for the *d*-type polarization functions added to the (O/7,3) basis set and the *p*-type polarization functions added to the (H/4) basis set were the optimum values found by Roos and Siegbahn [11], viz. 1.325 and 0.789, repsectively.

The calculations with the (5,2/2)→⟨2,1/1⟩ basis set were performed on an IBM 7094 computer using Version 2 of IBMOL [17, 18] (QCPE 92); the calculations with the (7,3/4)→⟨4,2/2⟩ basis set were performed on an IBM 360/75 computer using Version 4 of IBMOL [19]; all other energy calculations were performed on the 360/75 using the REFLECT program of Siegbahn [20]. Mulliken population analyses and dipole moment calculations were performed with the POPUL programs of Veillard [19]. Some times required for the calculation of the total energy of a single geometrical conformation using different basis sets, programs, and computers are shown in Table 2.

Table 2. Calculation times[a] in minutes for H_2O_2 using various basis sets, programs, and computers

Basis set	No. Basis functions		IBMOL(2)[b]	IBMOL(4)[b]	REFLECT	
	Uncontracted	Contracted	(7094)	(360/75)	Non-planar case	Planar case
(5,2/2)→⟨2,1/1⟩	26	12	12.2			
(7,3/4)→⟨4,2/2⟩	40	24	39.7	5.5		2.3
(7,3/4,1)→⟨4,2/2,1⟩	46	30			5.9	4.2
(7,3,1/4,1)→⟨4,2,1/2,1⟩	58	42		81.0	24.5	14.8

[a] CPU time except for 7094 which is elapsed time.
[b] IBMOL calculation times are for the non-planar case.

The search for optimum values for the geometrical parameters was conducted by varying the O–O and O–H bond lengths and the OOH bond angle in turn, holding all other parameters constant, and then fitting the calculated total energies to a quadratic or cubic equation. The optimum value thus found for one parameter was used as the constant value during the variation of the next parameter. In some cases, more than one cycle of variation of parameters was necessary to attain total energy constancy to eight figures.

Results and Discussion

The optimum values for the bond lengths and bond angle calculated with the different basis sets are given in Table 3. The values are seen to be highly dependent upon the basis set used.

The (5,2/2) basis set yields an O–O bond length that is 0.060 Å less than the experimental value and an O–H bond length that is 0.088 Å greater than the experimental value. Upon going to the (7,3/4) basis set, both these values improve significantly (errors equal to +0.006 Å and +0.024 Å, respectively). Addition of *p*-type functions to the H atoms brings the O–H bond length in very close agreement with the experiment value (error = 0.004 Å) and, as expected, has negligible effect upon the already good O–O bond length. Further addition of *d*-type functions to the O atom leaves the O–H bond length virtually unchanged, but reduces the O–O bond length to a value even less than that obtained with the (5,2/2) basis set.

The agreement of calculated bond angles with experiment is not very good in any case. All values are 5–7° too large which corresponds to a misplacement of the hydrogen atoms by about 0.1 Å. The range of the calculated values is about the same as the range of experimental uncertainty and corresponds to a range of misplacement of the hydrogen atoms by about ±0.015 Å, somewhat less than the range of the calculated values for the bond lengths.

These results are in general agreement with the conclusions of other workers [8–10, 24–26] – that calculations can be carried out using small basis sets to obtain bond lengths which agree with experimental values to within a few percent.

Table 3. Optimum geometries calculated for H_2O_2 with different basis sets

Parameter	Basis set	$\varphi = 120°$	$\varphi = 180°$	$\Delta[(\varphi = 120°) - (\varphi = 180°)]$
O–O	(5,2/2)	1.4145 Å	1.4228	−0.0103
	(7,3/4)	1.4812	1.4865	−0.0053
	(7,3/4,1)	1.4819	1.4876	−0.0057
	(7,3,1/4,1)	1.4038	1.4148	−0.0110
	(11,7,1/6,1)[a]	1.475[b]	1.475[b]	0.000
	Experimental	1.475 ± 0.004[c]		
O–H	(5,2/2)	1.0383	1.0339	+0.0044
	(7,3/4)	0.9739	0.9722	+0.0017
	(7,3/4,1)	0.9464	0.9458	+0.0006
	(7,3,1/4,1)	0.9442	0.9435	+0.0007
	(11,7,1/6,1)[a]	—	—	—
	Experimental	0.950 ± 0.005[c]		
$\sphericalangle$ OOH	(5,2/2)	101.85	100.22	+1.63
	(7,3/4)	100.63	99.43	+1.20
	(7,3/4,1)	99.64	98.66	+0.98
	(7,3,1/4,1)	101.11	99.71	+1.40
	(11,7,1/6,1)[a]	101.3[b]	100.2[b]	+1.1
	Experimental	94.8 ± 2.0[c]		

[a] (11,7,1/6,1)→⟨5,3,1/3,1⟩ [6].

[b] Veillard [6].

[c] Redington *et al.* [21].

Table 4a. Total energies[a] calculated for H_2O_2 with various basis sets and geometries

Basis set used for		$\varphi = 120°$	$\varphi = 180°$	$\Delta[(\varphi = 120°) - (\varphi = 180°)]$
Energy calculation	Geometry optimization			
(5,2/2)	(5,2/2)	−149.63690	−149.63643	−0.00047
	(11,7,1/6,1)[b]	−149.61610	−149.61735	+0.00125
(7,3/4)	(5,2/2)	−150.52717	−150.52895	+0.00178
	(7,3/4)	−150.53710	−150.53822	+0.00112
	(11,7,1/6,1)[b]	−150.53600	−150.53718	+0.00118
(7,3,1/4,1)	(5,2/2)	−150.59173	−150.59163	−0.00010
	(7,3/4)	−150.60217	−150.60149	−0.00068
	(7,3,1/4,1)	−150.60673	−150.60573	−0.00100
	(11,7,1/6,1)[b]	−150.60396	−150.60349	−0.00047
(11,7,1/6,1)[b]	(11,7,1/6,1)[b]	−150.79922[c]	−150.79832[c]	−0.00090[c]
Experimental				−0.00175[d]

Table 4b

(7,3/4,1)	(5,2/2)	−150.55618	−150.55764	+0.00146
	(7,3/4)	−150.57360	−150.57395	+0.00035
	(7,3/4,1)	−150.57527	−150.57548	+0.00021
	(11,7,1/6,1)	−150.57501	−150.57513	+0.00012
(7,3,1/4,1)	(7,3/4,1)	−150.60386	−150.60299	−0.00087
	(7,3,1/4,1)	−150.60673	−150.60573	−0.00100

[a] Energies in hartrees.

[b] $(11,7,1/6,1) \rightarrow \langle 5,3,1/3,1 \rangle$ [6].

[c] Veillard [6].

[d] Hunt *et al.* [22].

The (7,3/4,1) basis set, which is about the smallest "balanced" basis set one could construct to include *p*-type functions on the hydrogen atoms (cf. Roos and Siegbahn [11]), seems particularly good for this purpose. Also in agreement with the work of others [9, 24–26] we observe difficulty in calculating values for bond angles which agree well with experiment, even with the use of large basis sets.

Our primary interest, however is not the extent to which these optimum geometrical parameters agree or fail to agree with experiment, but the usefulness of the optimum values obtained with one basis set as geometrical parameters in an energy calculation with another basis set. Some total energies calculated for H_2O_2 in its skew conformation ($\varphi = 120°$) and in its trans-planar conformation ($\varphi = 180°$) using several basis sets and the optimum geometrical parameters obtained with the same and other basis sets are shown in Table 4a.

For any basis set, the lowest energy is calculated, of course, with the geometrical parameters as optimized with that same basis set. The improvement of total energies with increasing size and flexibility of the basis set also follows the well-known pattern. The last column in Table 4a gives the difference in total energy between the two conformations, i.e., the trans rotational barrier. Of particular interest is the observation that with the (7,3/4) basis set the energy of the 120° conformation is greater than the energy of the 180° conformation and, hence,

Table 5. Effect of polarization functions on the total energy[a] calculated for H_2O_2

Basis set	$\varphi = 120°$ [b]	$\varphi = 180°$ [b]	$\Delta[(\varphi = 120°) - (\varphi = 180°)]$
(7,3/4)	-150.53710	-150.53822	$+0.00112$
(7,3/4,1)	-150.57360	-150.57395	$+0.00035$
(7,3,1/4)	-150.58018	-150.57983	-0.00035
(7,3,1/4,1)	-150.60217	-150.60149	-0.00068

[a] Energies in hartrees.

[b] Geometry used for all calculations was the optimum geometry calculated with the (7,3/4) basis set.

no barrier to rotation is calculated, no matter which set of geometrical parameters is used; with the (7,3,1/4,1) basis set, however, a barrier to rotation is calculated, no matter which set of geometrical parameters is used. The best value for the barrier (obtained by using the (7,3,1/4,1) basis set for both optimization and energy calculations) is 57% of the experimental value and is the best value reported to date, though the improvement over Veillard's value (which is believed to approach the Hartree-Fock limit) should be regarded as accidental. Thus, at this level of refinement, we conclude that improvement of the basis set (especially by inclusion of polarization functions) is more important for calculation of the rotational barrier in hydrogen peroxide than the use of carefully optimized geometries.

Additional calculations were performed to determine the relative effects of the addition of *p*-type functions on the hydrogen atoms and *d*-type functions on the oxygen atoms. The optimum geometry as determined with the (7,3/4) basis set was used for all calculations. From the results (Table 5), it can be seen that using either *p*-type functions on the hydrogen atoms or *d*-type functions on the oxygen atoms will provide about two-thirds of the improvement in the total energy to be gained by using both types of polarization function together. However, the addition of *d*-type functions on the oxygen atoms alone results in an improvement in the energy difference equal to 82% of the amount to be gained by using both types of function, while use of *p*-type functions on the hydrogen atoms alone results in only 43% of the total improvement and the energy difference still has the wrong sign. Although the total energy of the molecule is determined by interactions among all four centers and improvement of the wave function in any region of the molecule must result in a lowering of the total energy, it is quite consistent with our ideas about localized chemical bonds that the greatest information about the potential function for rotation about the O–O "bond" can be gained by improving the wave function in this region.

These conclusions are further justified by the results of the Mulliken population analyses shown in Table 6a. All of these properties except the O–O overlap population are essentially an expression of the distribution of electronic charge between the hydrogen and the oxygen atoms. The *p*-type functions already included on the oxygen atoms provide sufficient flexibility for good charge distribution in this region and the greatest improvement is to be gained by addition of *p*-type orbitals on the hydrogen atoms. Addition of *d*-type functions to the oxygen atoms does not change the oxygen-hydrogen sharing, but only changes the distribution along the O–O bond. The effect of redistribution of

Table 6a. Population analyses for H_2O_2 calculated with various basis sets

Basis set used for		$\varphi = 120°$							$\varphi = 180°$						
Calculation	Geometry optimization	$n(H)$[a]	$n(O)$	$o(OH)$[b]	$o(OO)$	$q(H)$[c]	$q(O)$	μ[d]	$n(H)$	$n(O)$	$o(OH)$	$o(OO)$	$q(H)$	$q(O)$	μ
(5,2/2)	(5,2/2)	0.542	7.727	0.271	0.234	+0.209	−0.209	1.686	0.529	7.738	0.273	0.227	+0.217	−0.217	0.000
(7,3/4)	(7,3/4)	0.385	7.997	0.258	0.145	+0.377	−0.377	2.057	0.374	8.002	0.261	0.142	+0.384	−0.384	0.000
(7,3/4,1)	(7,3/4)	0.521	7.758	0.305	0.166	+0.201	−0.201	0.751	0.509	7.759	0.310	0.164	+0.205	−0.205	0.000
(7,3,1/4)	(7,3/4)	0.372	7.992	0.259	0.154	+0.387	−0.387	0.725	0.363	7.997	0.261	0.152	+0.392	−0.392	0.000
(7,3,1/4,1)	(7,3,1/4,1)	0.488	7.770	0.325	0.144	+0.212	−0.212	1.734	0.478	7.772	0.328	0.142	+0.217	−0.217	0.000

Table 6b

(7,3/4,1)	(7,3/4,1)	0.532	7.729	0.312	0.171	+0.183	−0.183	1.869	0.520	7.732	0.317	0.168	+0.189	−0.189	0.000
(7,3,1/4,1)'	(7,3/4,1)	0.486	7.751	0.319	0.165	+0.214	−0.214	1.729	0.478	7.755	0.322	0.163	+0.219	−0.219	0.000

[a] Net atomic population

[b] Overlap population.

[c] Gross atomic charge.

[d] Dipole moment in Debyes. Experimental values reported, 2.26 D, 3.15 D, [23, 22].

charge along this bond is little betrayed in the O–O overlap population but is seen in the decrease in the total energy and the sensitivity of the total energy to changes – i.e., rotation – in the O–O bond region.

These results suggest that a small basis set including *p*-type functions on hydrogen atoms but not *d*-type functions on first-row atoms could, indeed, be used for exploration of the potential surface as a function of geometrical distortions and for calculations of electron distribution in molecules involving only hydrogen and first-row atoms. Baird [10] has reached a similar conclusion regarding the use of the Pople-type STO 2G basis set for determining bond lengths, but a basis set including the flexibility of *p*-type functions on the hydrogen atoms, which the STO 2G set does not include, ought to be considerably superior. Pedersen and Morokuma [4] have noted that "hydrogen atom polarization appears to be significant for hydrogen peroxide and may be important for other molecules as well" and Forsén and Roos [7] used the (7,3/4,1) basis set to determine potential energy surfaces for HCO^+ and N_2H^+. Since the inclusion of these functions adds so little to the computation, there seems to be little justification for their continued exclusion in calculations using basis sets consisting of two contracted functions per atomic orbital.

These conclusions were further tested and borne out in the case of H_2O_2 with a complete set of calculations using the (7,3/4,1) basis set, the results of which are given in Tables 4b and 6b. With only the *p*-type polarization functions on the hydrogen atoms, the calculated barriers are bad, irrespective of the geometry; but the optimum geometry and the electron populations calculated with this basis set agree well with the results of calculations with larger basis sets. The use of the optimum geometry as determined with the (7,3/4,1) basis set in energy calculations with the (7,3,1/4,1) basis sets gives total energies within 0.00287 hartrees (1.80 kcal/mole) and a barrier energy within 0.00013 hartree (0.08 kcal/mole) of the best result obtained by optimizing the geometry with the (7,3,1/4,1) basis set itself.

The role of *d*-orbitals in bonds between first-row atoms is not sufficiently clarified in this study. Heteronuclear molecules such as H_2CNH ought to be examined more closely. Unfortunately Lehn *et al.* [27] have not included polarization functions in their basis sets for the study of the isoelectronic series H_2CCH^-, H_2CNH, H_2COH^+. The unusually bad value obtained for the O–O bond length in H_2O_2 when optimized with the (7,3,1/4,1) basis set indicates the need for better scaling. Roos and Siegbahn [11] have obtained their 3*d* orbital exponents for first and second-row atoms by minimization of the total energy alone. They have shown that, for first-row atoms, the total energy is only slightly dependent upon the value of the 3*d* orbital exponent, whereas gross atomic charge is highly dependent upon the value of the 3*d* exponent. Thus, charge distribution and other properties could also be important for choosing values for polarization exponents.

Conclusions

For small molecules involving only hydrogen and first-row atoms, Gaussian basis sets contracted to two functions per atomic orbital can effectively be used for the determination of equilibrium geometries and calculations of charge distribution. The (7,3/4,1) basis set, which is about the smallest balanced basis set which can be contructed to include *p*-type functions on the hydrogen atoms is particularly recommended. Inclusion of *p*-type functions on hydrogen atoms increases the complexity of the calculation very little, but results in a great improvement in the electron distribution in the X–H region (X is a first-row atom) and a significant improvement in the total energy.

In hydrogen peroxide (and probably in other molecules with first-row atoms bonded to each other), the inclusion of *d*-type functions on the oxygen atoms is essential for calculation of rotational potential barriers. The choice of a value for the 3*d* orbital exponent appears to be quite important, though the method of selection of good values is not yet clear.

In the calculation of small barriers to internal rotation, such as the trans barriers in hydrogen peroxide, some optimization of geometry is necessary so that the barrier is not obscured by gross errors. However, careful optimization of geometry is of secondary importance to the proper use of *d*-type polarization functions on the first-row atoms. For calculations approaching the Hartree-Fock limit, careful optimization of geometrical parameters is still necessary.

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