

## Gradient optimization of polarization exponents in *ab initio* MO calculations on $\text{H}_2\text{SO} \rightarrow \text{HSOH}$ and $\text{CH}_3\text{SH} \rightarrow \text{CH}_2\text{SH}_2$

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**Summary.** Analytical gradients were used to optimize the polarization function exponents in the 6-31G(*d*) and 6-31G(*d, p*) basis sets for the reactants, transition structures and products in the reactions  $\text{H}_2\text{SO} \rightarrow \text{HSOH}$  and  $\text{CH}_3\text{SH} \rightarrow \text{CH}_2\text{SH}_2$ . The optimized *d* exponents on the heavy atoms change by  $\pm 10\%$  in the course of the reactions and depend on the bonding of the heavy atoms. The *p* exponents on the hydrogens change by as much as a factor of 5 and depend on the element to which the hydrogen is bonded and its valency. The effect of exponent optimization on the relative energies is small ( $\pm 3$  kcal/mol). With the 6-31G(*d, p*) basis set, optimization of the polarization exponents can make some of the bonds significantly more polar, as judged by the Mulliken charges.

**Key words:** Exponents — Optimization — MO — Gradient — *Ab initio*

### introduction

In *ab initio* LCAO-MO calculations, the total energies and molecular properties depend strongly on the choice of atomic basis sets. Computational economy imposes serious restrictions on the number and types of functions that can be included in a basis set. Thus, considerable care is needed in choosing a basis set small enough to be computationally practical, yet flexible enough to describe the chemistry correctly. A number of recent reviews are available on the construction and selection of basis sets for MO calculations [1, 2]. Most basis sets currently in general use are obtained by minimization of the total energy for atoms [1, 2], with possibly some adjustment for the average molecular environment (e.g. [3]). Even for atoms, basis set optimization is very tedious and is best done using analytical gradients. Early examples of exponent derivative calculations include [4–6]; more recent gradient based exponent optimizations are reviewed in [7]. Lately, quasi-Newton methods with analytical second derivatives have been used to improve the efficiency of exponent optimizations

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[7]. For molecules, the question of balance between basis sets for different atoms in the molecule further complicates the optimization problem. For example, optimizing the basis functions for only one atom will improve the total energy, but may degrade some of the calculated molecular properties [8–11]. Basis sets for molecules are often extended by adding polarization functions and/or diffuse functions to atomic basis sets [1, 2]. These cannot be optimized readily for atoms alone, but must be chosen based on molecular calculations.

There have been several studies involving direct exponent optimization in molecules [1–3, 8–11]—a few carried out full optimizations, some optimized subsets of the exponents (e.g. valence shells, polarization functions) and others varied fixed distributions of exponents. So far, only one study has used analytical gradients to optimize exponents for molecular calculations [11]. The purpose of the present note is to examine the effects of optimizing polarization function exponents in two simple reactions:



These reactions were chosen to highlight possible changes in the effect of the polarization functions in the course of the reaction. In the first reaction,  $d$  orbitals are necessary for a proper description of the hypervalent sulfur in  $\text{H}_2\text{SO}$  [12], but are much less important in the normal valent HSOH. In the second example, the carbon and sulfur are neutral in the reactant thiol, but are formally charged in the product ylide ( $d$  orbitals are also needed for a correct description of the bonding in the ylide [13]). Both charge and valency should affect the optimized values of the exponents. There is also a question of whether the partial bonding in the transition states affects the optimal values of the polarization exponents.

### Method

Analytical gradients of the molecular energy with respect to the basis set exponents can be calculated readily for  $s$ ,  $p$  and  $d$  type gaussians [14]. These codes have been incorporated in a local version of GAUSSIAN 88 [15]. For the present application, only the exponents of the uncontracted polarization functions of the 6-31G( $d$ ) and 6-31G( $d, p$ ) basis sets [3] were optimized. The logarithms of the exponents rather than the exponents themselves are the preferred coordinates for the optimization. The BFGS algorithm [16, 17] was used to carry out the minimization with respect to  $\ln \alpha_i$ , where  $\alpha_i$  are the exponents. The initial hessian can be taken as a unit matrix, but better convergence is obtained with a hessian computed by numerical differentiation of the analytical gradients. A trust radius [17] of  $5 \times 10^{-2}$  (with no updating) was used to control the step size when the hessian eigenvalues were smaller than  $5 \times 10^{-3}$ . The convergence threshold for the optimization was set at  $5 \times 10^{-5}$  for the root mean square of the energy derivatives with respect to  $\ln \alpha$ .

### Results

The reactions  $\text{H}_2\text{SO} \rightarrow \text{HSOH}$  and  $\text{CH}_3\text{SH} \rightarrow \text{CH}_2\text{SH}_2$  have been studied previously [12, 13]. The optimized geometries at the HF/6-31G( $d$ ) level with standard polarization exponents are shown in Figs. 1 and 2 and were used for all calculations. The optimized polarization exponents, energies and Mulliken charges are listed in Tables 1 and 2.

Table 1.  $\text{H}_2\text{SO} \rightarrow \text{TS} \rightarrow \text{HSOH}$  with standard and optimized polarization exponents

	Standard polarization exponents			Optimized polarization exponents		
	$\text{H}_2\text{SO}$	TS	HSOH	$\text{H}_2\text{SO}$	TS	HSOH
6-31G( $d$ ) basis						
$\alpha_s$	0.65	0.65	0.65	0.6023	0.5525	0.6092
$\alpha_o$	0.80	0.80	0.80	0.6834	0.5578	0.6956
$E_{\text{tot}}$	-473.438037	-473.352359	-473.489654	-473.439232	-473.356414	-473.490227
$E_{\text{rel}}$	0.00	53.76	-32.39	0.00	51.97	-32.00

Table 1.  $\text{H}_2\text{SO} \rightarrow \text{TS} \rightarrow \text{HSOH}$  with standard and optimized polarization exponents

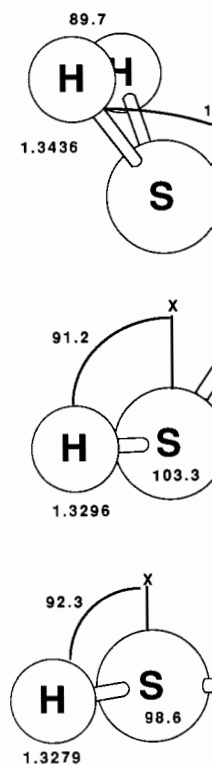
	Standard polarization exponents			Optimized polarization exponents		
	$\text{H}_2\text{SO}$	TS	HSOH	$\text{H}_2\text{SO}$	TS	HSOH
6-31G(d) basis						
$\alpha_S$	0.65	0.65	0.65	0.6023	0.5525	0.6092
$\alpha_O$	0.80	0.80	0.80	0.6834	0.5578	0.6956
$E_{\text{rot}}$	-473.438037	-473.352359	-473.489654	-473.439232	-473.356414	-473.490227
$E_{\text{rel}}$	0.00	53.76	-32.39	0.00	51.97	-32.00
$q_S$	0.668	0.260	0.230	0.638	0.219	0.215
$q_O$	-0.742	-0.749	-0.780	-0.730	-0.755	-0.778
$q_{\text{H}_1}$	0.036	0.098	0.079	0.046	0.117	0.088
$q_{\text{H}_2}$	0.036	0.390	0.471	0.046	0.418	0.475
6-31G(d, p) basis						
$\alpha_S$	0.65	0.65	0.65	0.6818	0.6392	0.6660
$\alpha_O$	0.80	0.80	0.80	0.6650	0.5956	0.6372
$\alpha_{\text{H}_1}$	1.10	1.10	1.10	0.2201	0.2021	0.5726
$\alpha_{\text{H}_2}$	1.10	1.10	1.10	0.2201	0.6169	0.9969
$E_{\text{rot}}$	-473.445059	-473.363168	-473.499971	-473.450750	-473.367682	-473.501233
$E_{\text{rel}}$	0.00	51.39	-34.46	0.00	52.13	-31.68
$q_S$	0.771	0.348	0.277	1.233	0.586	0.370
$q_O$	-0.746	-0.733	-0.681	-0.755	-0.737	-0.683
$q_{\text{H}_1}$	-0.012	0.050	0.037	-0.239	-0.132	-0.034
$q_{\text{H}_2}$	-0.012	0.036	0.368	-0.239	0.283	0.348

Total energies in hartree, relative energies in kcal/mol; all calculations at the HF/6-31G(d) (standard exponents) optimized geometry ( $\text{H}_1$  is attached to S,  $\text{H}_2$  moves from S to O during the course of the reaction)

Table 2.  $\text{CH}_3\text{SH} \rightarrow \text{TS} \rightarrow \text{CH}_2\text{SH}_2$  with standard and optimized polarization exponents

	Standard polarization exponents			Optimized polarization exponents		
	$\text{CH}_3\text{SH}$	TS	$\text{CH}_2\text{SH}_2$	$\text{CH}_3\text{SH}$	TS	$\text{CH}_2\text{SH}_2$
<b>6-31G(d) basis</b>						
$\alpha_C$	0.80	0.80	0.80	0.6983	0.5521	0.7488
$\alpha_S$	0.65	0.65	0.65	0.5857	0.4920	0.5717
$E_{\text{tot}}$	-437.700319	-437.535775	-437.565571	-437.700991	-437.540025	-437.566813
$E_{\text{rel}}$	0.00	103.25	84.56	0.00	101.01	84.20
$q_C$	-0.628	-0.459	-0.777	-0.627	-0.532	-0.752
$q_S$	-0.061	-0.250	0.261	-0.086	-0.303	0.208
$q_{\text{H}_1}$	0.198	0.196	0.201	0.199	0.224	0.201
$q_{\text{H}_2}$	0.198	0.189	0.185	0.199	0.219	0.185
$q_{\text{H}_3}$	0.090	0.120	0.065	0.098	0.141	0.080
$q_{\text{H}_4}$	0.202	0.204	0.065	0.202	0.235	0.080
<b>6-31G(d, p) basis</b>						
$\alpha_C$	0.80	0.80	0.80	0.6632	0.5668	0.6448
$\alpha_S$	0.65	0.65	0.65	0.6414	0.6187	0.6394
$\alpha_{\text{H}_1}$	1.10	1.10	1.10	1.2122	1.1157	1.1206
$\alpha_{\text{H}_2}$	1.10	1.10	1.10	1.2122	1.1157	1.1579
$\alpha_{\text{H}_3}$	1.10	1.10	1.10	0.6363	0.6425	0.6404
$\alpha_{\text{H}_4}$	1.10	1.10	1.10	1.1726	0.5410	0.6409
$E_{\text{tot}}$	-437.709026	-437.549745	-437.576316	-437.709899	-437.552902	-437.577338
$E_{\text{rel}}$	0.00	99.95	83.28	0.00	98.52	83.18
$q_C$	-0.487	-0.348	-0.684	-0.545	-0.380	-0.726
$q_S$	-0.018	-0.167	0.364	0.046	-0.044	0.508
$q_{\text{H}_1}$	0.151	0.148	0.151	0.167	0.174	0.157
$q_{\text{H}_2}$	0.151	0.142	0.135	0.167	0.169	0.143
$q_{\text{H}_3}$	0.048	0.075	0.017	-0.005	0.026	-0.041
$q_{\text{H}_4}$	0.155	0.151	0.017	0.169	0.055	-0.041

Total energies in hartree, relative energies in kcal/mol; all calculations at the HF/6-31G(d) (standard exponents) optimized geometry ( $\text{H}_1$  and  $\text{H}_2$  are attached to C,  $\text{H}_3$  is attached to S,  $\text{H}_4$  moves from C to S during the course of the reaction)



For both the 6-31G(d) and 6-31G(d, p) basis sets, the transition state structure is similar to that of the reactant and product. The changes in the lengths of the sulfur-hydrogen bonds in the transition state are much larger than those of the sulfur-hydrogen bonds in the reactant and product. The changes in the lengths of the sulfur-hydrogen bonds in the transition state are much larger than those of the sulfur-hydrogen bonds in the reactant and product. The changes in the lengths of the sulfur-hydrogen bonds in the transition state are much larger than those of the sulfur-hydrogen bonds in the reactant and product.

Similar to  $\text{H}_2\text{SO}$ , the transition state that is formed by the hydrogen involved in the reaction. The changes in the lengths of the sulfur-hydrogen bonds in the transition state are much larger than those of the sulfur-hydrogen bonds in the reactant and product.

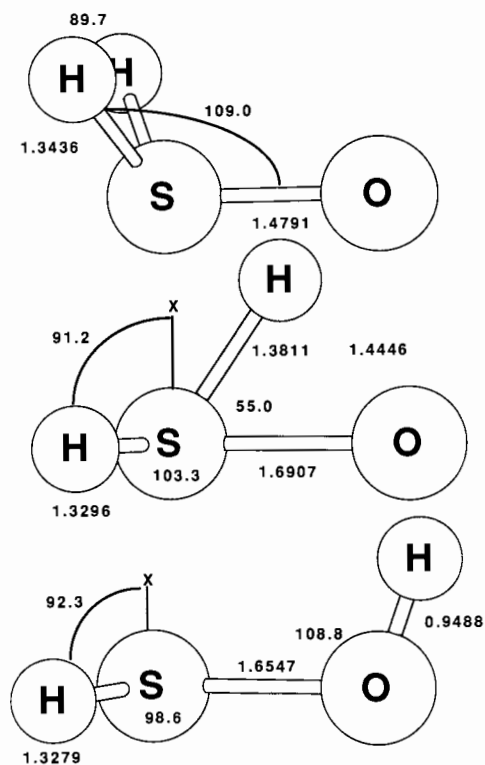
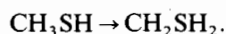
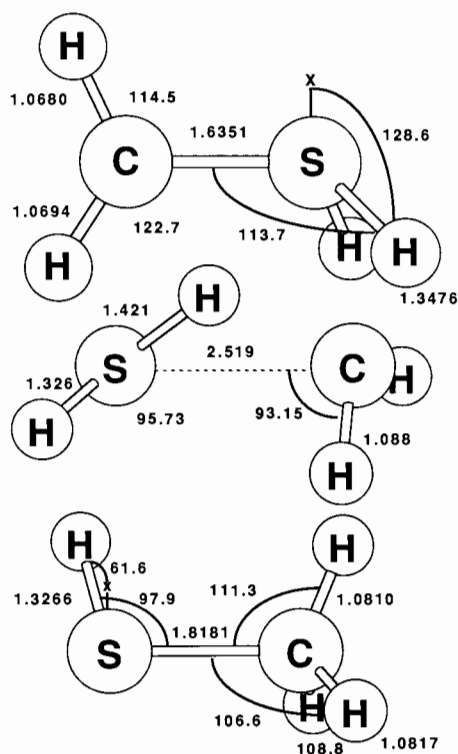


Fig. 1. Geometries of reactant, transition state and product for  $\text{H}_2\text{SO} \rightarrow \text{HSOH}$  optimized at the HF/6-31G(*d*) level with standard exponents

For both the 6-31G(*d*) and 6-31G(*d, p*) basis sets, the optimized *d* exponents for sulfur in the reactant and product are quite similar to each other, but the exponent in the transition structure is ca. 10% smaller. This may reflect the partially broken/partially formed bonds in the transition state. The changes in the oxygen *d* exponent parallel those of the sulfur. In the 6-31G(*d, p*) basis set, the optimized exponents for the hydrogen *p* orbitals are 2–5 times smaller than the values assigned in the standard basis set. The changes in the *p* exponent of the hydrogen migrating from sulfur to oxygen ( $\text{H}_2$ ) is much larger than for the hydrogen that remains on sulfur ( $\text{H}_1$ ); however, the exponent for  $\text{H}_1$  depends on whether the sulfur is hypervalent or not. This suggests that the *p* functions on hydrogen are being used to correct deficiencies in the basis set of the adjacent heavy atom. Despite the sizeable changes in the exponents, optimization changes the relative energies of reactants, transition state and products by only 1–3 kcal/mol. For the 6-31G(*d*) basis set, optimization of the *d* functions does not change the Mulliken charges significantly. However, with the 6-31G(*d, p*) basis, optimization of the *p* functions on hydrogen results in a marked polarization of the S—H bond.



Similar to  $\text{H}_2\text{SO}$ , the polarization exponents for the heavy atoms are smaller in the transition state than in the reactant or the product. Likewise, the *p* exponent on the hydrogen involved in the 1, 2 shift ( $\text{H}_4$ ) changes the most. Differences in the relative energies on optimization are small for both basis sets. Optimization of the polarization exponents causes the C—S bond to become significantly more polarized for the 6-31G(*d, p*) basis but not for the 6-31G(*d*) basis.



**Fig. 2.** Geometries of reactant, transition state and product for  $\text{CH}_3\text{SH} \rightarrow \text{CH}_2\text{SH}_2$  optimized at the HF/6-31G(*d*) level with standard exponents

## Conclusions

The optimized *d* exponents in the simple systems considered in this paper are 5%–20% lower than the values in the standard 6-31G(*d*) basis set and vary by  $\pm 10\%$  from structure to structure. The optimized *d* exponents in the transition states are generally smaller than in the equilibrium structures, possibly reflecting the bond making/breaking occurring in the transition state. On the other hand, the *p* exponents for the hydrogens differ from the value assigned in the standard basis set by up to a factor of 5. The optimized values for the *p* exponents depend strongly on the element to which the hydrogen is bonded and also the valency of that element. The effect of optimization of the polarization exponents on the relative energies is comparatively small. For the 6-31G(*d, p*) basis set (but not the 6-31G(*d*) basis), some bonds become significantly more polar when the polarization functions are optimized. Exponent optimization is a rather costly means of improving a wavefunction; hence it is probably more economically to expand the basis set rather than optimize the basis set parameters for routine MO calculations. Nevertheless, exponent optimizations may be useful in selected cases to test for deficiencies in the basis sets.

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