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# A basis set study of the NMR chemical shift in $\text{PH}_3$

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Chemical shift calculations varying the heavy atom valence shell basis functions have been carried out for  $\text{PH}_3$  as a prototype molecule containing second row atoms. A triple valence split with two sets of  $d$  polarization functions,  $(66211/6211/11) = [5s, 4p, 2d]$ , appears to be adequate for second-row atoms in the GIAO-SCF approach. Chemical shift calculations on  $\text{SiH}_4$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$  as well as  $\text{PH}_3$  employing this basis yield results in good agreement with experiment and with calculations of others involving larger bases. Bond length and bond angle shift derivatives in these hydrides are negative, continuing the general trend observed before for molecules containing first-row atoms.

## INTRODUCTION

Since the chemical shift in magnetic resonance is such a small and sensitive effect it has only been recently with larger and faster computers and their ability to handle large basis sets that reasonably accurate theoretical calculations have been forthcoming. It would be extremely advantageous to discover reasonably small and efficient basis sets that would allow one to study the basic causes of chemical shifts without demanding basis sets and computer facilities of extreme size. We have recently found that basis sets of the type  $(6311/311/1) = [4s, 3p, d]^1$  for nonhydrogen atoms and  $(31) = [2s]$  for hydrogen are reasonably efficient for the accurate calculation of the chemical shift in a GIAO-SCF approach for small first-row molecules.<sup>2,3</sup> Chemical shifts and shift anisotropies using this intermediate size basis agree as well with experiment as other conventional SCF approaches using more extensive basis sets such as those of Lazeretti and Zanasi<sup>4</sup> and Höller and Lischka,<sup>5</sup> are comparable to SCF modifications such as Schindler and Kutzelnigg's IGLO method<sup>6-8</sup> and Hansen and Bouman's random phase approximation,<sup>9</sup> and are an improvement on the smaller sets used by Rohlfing, Allen, and Ditchfield.<sup>10</sup> A combination of the GIAO approach<sup>11</sup> and efficient bases allow a variety of studies on the chemical shift including the effects of geometry.<sup>2</sup> It was shown that nearly all shift first derivatives are negative with respect to bond lengthening, suggesting negative temperature coefficients. Modifications to our primary basis set indicated that the addition of a second set of  $d$  polarization functions was probably not necessary for first-row atoms but that the addition of diffuse  $s$  and  $p$  functions might be required for a more accurate characterization of such molecular species, especially those involving nitrogen, oxygen, and fluorine.

The purpose of the present paper is to report on a study of basis set effects on the chemical shift of  $\text{PH}_3$  as a prototype molecule containing a second-row atom. Phosphorus is an element of considerable chemical interest and its simple hydride can be treated with a basis set small enough to allow a great variety of calculations to be performed. It is found basically that, just as was the case for first-row atoms, a triple valence split with polarization is probably adequate for

phosphorus and for second-row atoms in general in the GIAO approach but that two sets of  $d$  polarization functions are required rather than the single set found for the first row atoms. Calculations employing our second-row primary basis (*vide infra*) have been carried out on  $\text{SiH}_4$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$  as well as  $\text{PH}_3$  and the dependence of these shifts on bond length and bond angle has been determined.

## CALCULATIONS

Calculations were carried out on a DEC VAX 11/730 computer using Ditchfield's perturbed Hartree-Fock GIAO approach.<sup>11</sup> The calculations correspond to an isolated molecule with fixed nuclei; the experimental molecular geometries employed were taken from Refs. 12 and 13 where  $r_e$ ,  $r_s$ , or  $r_0$  structures were used, in this order of preference. Absolute chemical shifts are calculated and compared with appropriate experimental data using units of ppm (parts per million). Estimates of the first and second bond length derivatives of the chemical shift ( $\sigma'_r$  and  $\sigma''_r$ ) were obtained by lengthening and shortening appropriate bonds by 0.01 Å from their experimental length; the effect on the chemical shift of angle distortion  $\sigma'_\theta$  was investigated by carrying out shift calculations in which all bond angles were symmetrically modified by  $\pm 3^\circ$  about the experimental bond angle.

The  $(6311/311/1) = [4s, 3p, d]$  bases of Krishnan, Binkley, Seeger, and Pople<sup>14</sup> were employed for first-row atoms with the  $(31) = [2s]$  basis for hydrogen taken either from Ditchfield, Hehre, and Pople<sup>15</sup> or the virtually identical set due to Tatewaki and Huzinaga.<sup>16</sup> For second row atoms the 6-31G\* basis sets due to Francel *et al.*<sup>17</sup> were used including polarization functions ( $d$  functions for the second row atoms) and the diffuse  $s$  and  $p$  functions of Clark, Chandrasekhar, Spitznagel, and von Schleyer.<sup>18</sup> All scale factors were set equal to unity. The Pople standard basis without polarization or diffuse functions in its  $(6631/631) = [4s, 3p]$  form was progressively increased in size by relaxing the threefold contraction in the valence shell to 2,1 and 1,1,1 forms. The progressive relaxation of this particular shell was done by freeing up initially that primitive with the lowest exponent while retaining the twofold contraction made up of those primitives with the two highest exponents,

and finally freeing all of the primitives in the original three-fold contraction.  $sp$ -diffuse functions were considered as well as multiple  $d$  polarization functions; the multiple  $d$  polarization functions were created from the original primitive by multiplying and dividing the original exponent by two as suggested by Frisch, Pople, and Binkley<sup>19</sup> so that the  $d$ -exponent ratios were always equal to four. For most of the calculations a  $(31) = [2s]$  basis was used for hydrogen although, as is discussed later, effects of some larger hydrogen bases were investigated.

## RESULTS AND DISCUSSION

### The triple-split-valence primary basis

Just as we concluded earlier that a triple-split-valence basis with a single set of (6)  $d$  polarization functions was adequate for first-row atoms,<sup>2</sup> we conclude here (*vide infra*) that a triple-split-valence basis is also adequate for second-row atoms of the form  $(66211/6211/11) = [5s, 4p, 2d]$  where two  $d$  polarization functions are required. We refer to this as our primary basis set for second-row atoms and use this as a "norm" in the discussions which follow.

In the present study we have basically varied the split of the valence shell, the number of  $d$  polarization functions used, and whether or not  $sp$ -diffuse functions are employed. In this regard, the notation employed by Frisch, Pople, and Binkley<sup>19</sup> is particularly appropriate for our discussions. The basis sets used by Pople and co-workers (and used here) indicate the general contraction of all inner shells, the contraction of the valence shell (shared  $s$  and  $p$  exponents), the presence of  $sp$ -diffuse functions (indicated by  $a +$  symbol) and the number of  $d$  polarization functions employed. We use both the standard and Pople notation reminding the reader that the heavy atom Pople notation does not usually apply to our hydrogen basis sets which, unless otherwise specified, are always of the  $(31) = [2s]$  type.

### Hydrogen basis

Our previous work<sup>2,3</sup> on first-row-atom molecules showed that the use of a simple  $(31) = [2s]$  basis for hydrogen was satisfactory for the calculation of the absolute chemical shift for the heavy atoms; furthermore, although one would not expect this to be an optimum basis for the hydrogen chemical shift, it was found that relative hydrogen shifts were given surprisingly well by this small set of functions. Using larger basis sets for hydrogen, possibly including  $p$  polarization functions, greatly increases the number of orbitals in a calculation and, accordingly, the time and computer memory required. In all of the calculations reported in the following sections the simple  $(31) = [2s]$  basis is employed for efficiency's sake. A variety of cases were studied comparing the hydrogen  $(311)$  and  $(31)$  bases with heavy atom double, triple, or quadruple valence splits and one or two  $d$  functions, and it was found that the difference in the shifts of the heavy atoms for these bases was only of the order of 1 or 2 ppm. Results employing our primary basis changing from a  $(31)$  to a  $(31/1)$  hydrogen basis with polarization showed an increase in the phosphorus chemical shift of 3.1 ppm and a decrease in the hydrogen chemical shift of 0.51 ppm. The original Pople basis  $(6631/631)$  with no diffuse or

polarization functions is more sensitive to the hydrogen basis used, the change from  $(31)$  to  $(311)$  for hydrogen resulting in a decrease of the phosphorus chemical shift of 8.0 ppm. This basis, however, is not a good one in any sense for phosphorus so its sensitivity to the hydrogen basis is not of concern. We conclude, therefore, that a hydrogen  $[2s]$  basis is adequate for molecular calculations involving atoms of the first or second row of the Periodic Table; it is likely not adequate for absolute calculations of the hydrogen chemical shift itself.

### Phosphorus in $\text{PH}_3$

The basis sets study data for  $\text{PH}_3$  in both its experimental pyramidal ( $C_{3v}$ ) and planar ( $D_{3h}$ ) forms are tabulated in Table I and presented graphically in Fig. 1. The bases studied here involve the 6-31G, 6-211G, 6-1111G  $sp$ -function bases, with or without  $sp$ -diffuse functions, and with from 0 to three sets of  $d$  polarization functions. The hydrogen basis used is held fixed at  $(31) = [2s]$ .

For the experimental pyramidal geometry of  $\text{PH}_3$ , a variety of conclusions can be reached. First of all, the data clearly show that the addition of the  $sp$ -diffuse functions has a relatively minor effect on the chemical shift. Changing the valence split [from (6-31G) to (6-211G) to (6-1111G)] has a large effect, and within each type of split valence set the effect of the addition of  $d$  orbitals is quite noticeable. The addition of the first set of  $d$  functions has a very large effect in all cases, while that of the addition of a second set is smaller but still significant; the addition of a third set of  $d$  polarization functions causes relatively minor changes, of the order of a few ppm, and in all likelihood does not present any great gain in the calculation of the shift, particularly in light of the increased size of the basis set required. Using the paramagnetic component of the chemical shift from the experimental work of Gierke and Flygare<sup>20</sup> and the diamagnetic component averaged from the theoretical calculations of Höller and Lischka<sup>5b</sup> and Lazeretti and Zanasi<sup>21</sup> one arrives at a "best" experimental chemical shift value for  $\text{PH}_3$  of 594 ppm, a result in rather good agreement with our 6-211G( $2d$ ) calculation.

Although the effect of added  $d$  functions seems to indicate a kind of convergence in the shift calculation, such is not the case with the general relaxation of the  $sp$ -valence functions. Some other representative calculations on  $\text{PH}_3$  shown in Table III are closer to the results we obtained for our 6-1111G( $2d$ ) set but the number of basis functions employed by these authors is larger. Since the effect of a few additional functions on each atom mounts as one goes from simple hydrides to more complicated structures and since we are looking for a relatively efficient basis to use for shift calculations we suggest that the triple-split-valence set without diffuse functions but with two sets of  $d$  polarization functions [the 6-211G( $2d$ ) set] is probably adequate for phosphorus and for second-row atoms in general. Until calculations can be carried out on larger systems, the question of whether or not it is necessary to go to the quadruple-split-valence set must remain unanswered.

From part 2 of Table I one can see that once at least one set of  $d$  polarization functions is included in the basis set the

TABLE I. Chemical shift  $\sigma$  (ppm) and shift anisotropy  $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$  (ppm) for phosphorus in  $\text{PH}_3$  for a variety of basis sets in both the experimental pyramidal  $C_{3v}$  and planar  $D_{3h}$  geometries. The experimental PH bond length was used in both forms. The number of  $d$  polarization sets is indicated by  $n$ .

	$C_{3v}$				$D_{3h}$			
	$n = 0$	1	2	3	$n = 0$	1	2	3
<i>sp</i> basis								
(1) $\sigma_p$								
6-31G	667.0	622.6	621.5	621.5	704.9	643.6	624.0	605.1
6-31 + G	665.0	620.1	618.2	618.5	706.7	645.0	625.0	608.9
6-211G	652.7	605.4	598.1	595.1	680.5	613.1	587.7	584.8
6-211 + G	655.2	608.1	601.3	598.9	689.7	623.6	598.7	594.3
6-1111G	632.5	584.2	578.6	576.5	665.1	596.0	571.7	563.9
6-1111 + G	633.9	585.6	580.3	578.5	672.9	604.3	580.6	572.3
(2) $\Delta\sigma_p$								
6-31G	-53.3	-39.6	-41.5	-38.0	-167.1	-208.7	-198.6	-189.5
6-31 + G	-43.2	-39.6	-41.7	-40.1	-179.5	-222.5	-213.0	-205.0
6-211G	-35.3	-30.4	-32.8	-34.1	-170.8	-213.1	-202.5	-201.5
6-211 + G	-38.1	-33.3	-35.7	-36.6	-181.7	-224.5	-216.8	-214.7
6-1111G	-38.6	-33.5	-35.9	-36.2	-179.8	-220.8	-210.8	-209.4
6-1111 + G	-40.4	-35.1	-38.1	-38.3	-191.3	-234.5	-225.4	-221.6

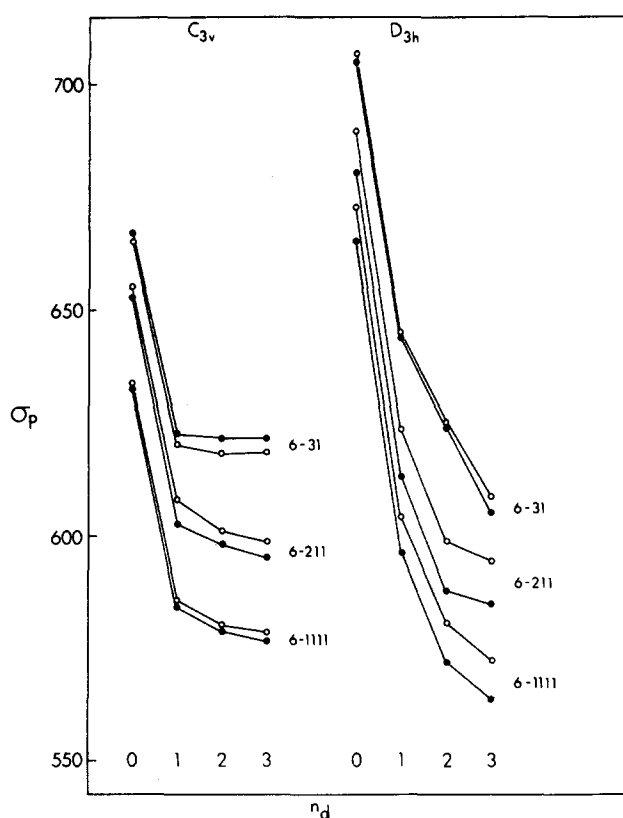


FIG. 1. Variation of the isotropic chemical shift in  $\text{PH}_3$  as a function of basis set for both pyramidal and planar structures. The basic *sp* contractions are indicated beside each line of data and correspond to the solid circle data; open circle data have one additional *sp*-diffuse set of functions. The number of sets of  $d$  polarization functions  $n_d$  is indicated below the appropriate points. The PH bond length was kept constant at its experimental value in these particular studies.

anisotropy is relatively insensitive to other basis set changes. The calculated anisotropy is only in modest agreement with experiment where values of  $-52^{20}$  and  $-55.5^{22}$  ppm are reported. Our results would seem to indicate that use of our primary basis set for second-row atoms [6-211G(2*d*)] may be adequate for calculational accuracy in the range of 10–20 ppm for second-row atoms involving single bonded species. Our prior work on first row atoms indicates that the accuracy there with a similar triple-split-valence primary basis set is probably of the order of 5–10 ppm for simple species. Since we are talking about an absolute chemical shift and since often only trends are desired in shift calculations, the results for various species may be better on a relative scale.

Although not tabulated we comment briefly on the energies and the hydrogen chemical shifts for the  $\text{PH}_3$  molecule in its experimental pyramidal geometry. One finds that in going from our smallest basis set (6-31G) to the largest one [6-1111 + G(3*d*)] the addition of a single set of  $d$  polarization functions obtains better than 87% of the maximum energy change. The addition of a second set of  $d$  polarization functions yields better than 91%–94% of the maximum energy change in the bases studied. These results are consistent with those of Magnusson and Schaefer<sup>23</sup> who in a study of some larger molecules as well as simple hydrides of the second-row atoms conclude that one and certainly two sets of  $d$  functions are adequate for most of the energy lowering due to the addition of polarization functions. It is interesting (and reassuring) to note the parallel between the number of sets of  $d$  functions needed for an adequate energy lowering and for an adequate determination of chemical shift. In our calculations the energy changes are dominated by the number of sets of  $d$  functions and show very little variation in terms of whether or not diffuse functions are added or whether the valence split is double, triple, or quadruple. The

effect on the hydrogen chemical shift is likewise only sensitive to the number of sets of  $d$  functions employed and in general shows very little variation over all of the sets studied. The hydrogen chemical shift for  $\text{PH}_3$  observed in the 6-31G basis is 31.31 ppm while that obtained for the largest basis employed [6-1111 +  $G(3d)$ ] is 30.20 ppm.

Because the effects of geometry on the calculated chemical shift are of interest the basis set study for  $\text{PH}_3$  was also carried out for the molecule in its planar  $D_{3h}$  state. The data are also given in Table I where the experimental pyramidal PH bond length is used for the planar form. For the planar form, provided at least a triple valence split is used two sets of  $d$  polarization functions are adequate but there is a much more noticeable effect from the  $sp$ -diffuse functions both in the shift and the shift anisotropy. Obviously, generalizations regarding the need to include various types of functions in calculations can be a function of the geometry of the molecule being studied.

An examination of the data in Table I shows that the change in the chemical shift going from the pyramidal to planar form depends upon the number of sets of  $d$  polarization functions employed. As the number of these sets is increased the change in the shift becomes less positive and finally becomes negative when two or three sets of  $d$  functions are used. The general trend observed might lead one to infer that the change in the shift in going from the pyramidal to the planar form should indeed be negative; however, it must be recalled that these calculations were carried out at a fixed, experimental pyramidal PH bond length. If the  $\text{PH}_3$  bond length is optimized<sup>24</sup> as a function of the HPH angle one finds that the bond length decreases monotonically as the angle is increased. If the optimized geometry is then employed for the planar case it is found for our primary basis set that the planar chemical shift is 606.2, a positive change of 8.1 ppm rather than a negative change at fixed  $r_e$  of -10.4 ppm. This predicted positive change is in good agreement with that calculated by Keil and Ahlrichs<sup>25</sup> of +11.7 ppm where these authors also employ a shorter bond length for the planar form. For our primary basis set with a fixed PH bond length the change in energy in going from pyramidal to planar forms is +0.0653 a.u. (41.0 kcal/mol) whereas when the optimized bond length is employed the barrier to inversion is 0.0636 a.u. (39.9 kcal/mol). Keil and Ahlrichs calculate an energy change of 0.0605 a.u. (38.0 kcal/mol). We note again, then, that the use of an optimized structure vs a nonoptimized one can also lead to changes in the calculated shift in the range of 10–20 ppm for  $\text{PH}_3$  as a simple prototype molecule containing a second-row atom.

The interpretation, then, of the change in the chemical shift in  $\text{PH}_3$  going from the pyramidal to the planar form is complicated by choice of basis and by whether or not one optimizes the bond length at the two geometries. Furthermore, attempting such an interpretation without knowledge of the shift surface in the vicinity of the structures in question is fraught with difficulties since a monotonic change in the shift between the two geometries is not at all obvious. Indeed, as can be seen from Fig. 2 the phosphorus chemical shift goes through a minimum in that region where the HPH angle varies from 80 to 120°. Using the 6-211G( $2d$ ) basis the

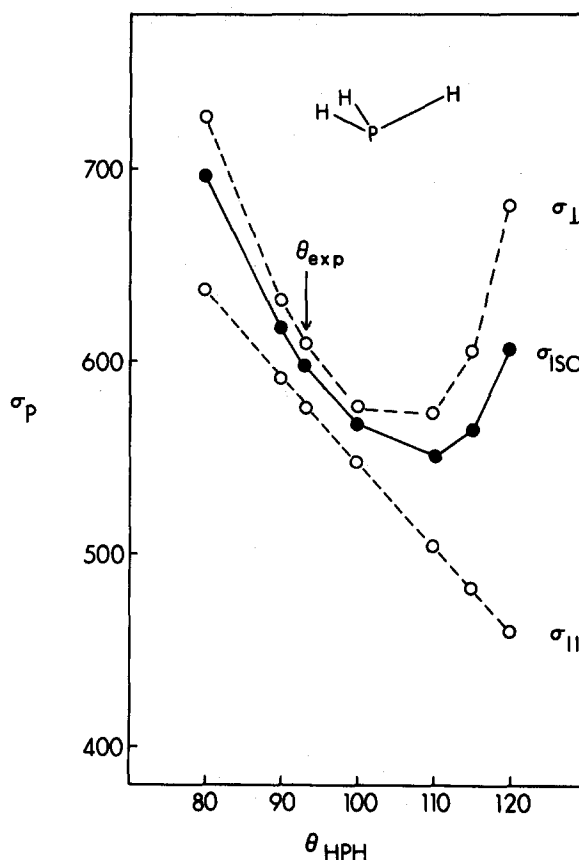


FIG. 2. Angular variation of the various shift components in  $\text{PH}_3$  as a function of the HPH angle. The PH bond length was optimized at each bond angle.

the bond lengths in  $\text{PH}_3$  were optimized at various angles in this range. While often SCF optimized geometries do not agree in detail with the experimental ones, here for this basis at the equilibrium bond angle (93.3°) the optimized bond length is 1.421 Å, in good agreement with the experimental one of 1.420 Å. Furthermore, a three-point fit near the energy minimum as calculated from our optimization studies shows that the SCF optimized bond angle is within 1.6° of that observed experimentally. Accordingly, we calculated the chemical shift over this range of angles using the optimized bond lengths and have compared these results to the shift calculated at a fixed (experimental) bond length in Table II. The calculated decrease of the equilibrium bond length as the molecule becomes planar agrees with intuitive feelings about hydrogen-hydrogen nonbonded repulsions. As seen in that table and in Fig. 2 the minimum in the isotropic chemical shift is caused by a quadratic-like behavior of the perpendicular component of the chemical shift, the parallel component showing essentially a decreasing linear dependence on bond angle. Figure 2 indicates that the derivative of the isotropic chemical shift with increasing bond angle is negative in the vicinity of the experimental geometry and the tabulated data in Table II also show that a decrease in the bond length causes an increase in the isotropic chemical shift; more data on shift derivatives is discussed in a later section. The hydrogen chemical shift shows essentially a linear dependence on the bond angle while the anisotropy  $\Delta\sigma$  is

TABLE II. The bond angle dependence of chemical shift properties of  $\text{PH}_3$  for fixed and optimized [6-211G(2d)] PH bond lengths. Shift data are in ppm.

$r = 1.420^a$		$r = r_{\text{opt}}$				
$\theta$	$\sigma$	$\sigma$	$r_{\text{opt}} (\text{\AA})$	$\Delta\sigma$	$\sigma_{\text{H}}$	$E(\text{a.u.})$
80	700.3	695.5	1.433	- 87.0	30.91	- 342.431 78
90	619.5	617.9	1.424	- 40.6	30.42	- 342.446 72
93.3 <sup>a</sup>	598.1	596.7	1.425	- 32.5	30.21	- 342.448 45
100	564.4	566.5	1.416	- 29.5	29.76	- 342.446 57
110	542.1	549.6	1.406	- 68.8	28.99	- 342.428 32
115	551.3	563.5	1.398	- 122.7	28.65	- 342.410 48
120	587.7	606.2	1.384	- 221.5	28.51	- 342.384 87

<sup>a</sup>  $\text{PH}_3$  experimental geometry:  $r_{\text{exp}} = 1.420\ 02\ \text{\AA}$ ,  $\theta_{\text{exp}} = 93.3454^\circ$ .

rather sensitive to geometry, particularly at the large bond angles where  $\sigma_1$  is changing so rapidly. The calculated increase in energy from the minimum energy is approximately 12.7 kcal/mol at an angle of  $110^\circ$ , so it seems likely that normal vibrations would keep the  $\text{PH}_3$  molecule in that region of its surface where both the angle and bond length derivatives of the chemical shift will be negative.

Calculations as a function of bond angle were also carried out for  $\text{H}_2\text{S}$  for the region of HSH angles from  $50$  to  $180^\circ$  using our primary 6-211G(2d) basis with optimized bond lengths.<sup>24</sup> The data are shown in Fig. 3 where it can be seen that the relatively slow variation of the isotropic chemical shift in the vicinity of the experimental geometry results

from an averaging of rather rapidly changing  $x$ ,  $y$ , and  $z$  components of the shift. Further discussion concerning the underlying causes for these geometry effects both for  $\text{H}_2\text{S}$  and  $\text{PH}_3$  must await studies in which a detailed partitioning of the shift components by atomic orbital and molecular orbital are carried out.

Finally, in Table III the results using our primary basis set at experimental geometries are compared to some other representative calculations. In general, all the calculations agree quite well with each other and, with the exception of the anisotropy in  $\text{PH}_3$ , quite well with experiment. Only in the case of Lazeretti and Zanasi<sup>21</sup> was energy data given which can be compared with that obtained in the present work. The much larger basis sets used by these authors yield significantly lower energies for the equilibrium geometries employed, an effect clearly to be expected. It is interesting to note that in each of the four molecules cited the difference in calculated energy between our data and that of Lazeretti and Zanasi is approximately of the same value, 0.039 a.u.

### Effects of differential bond length and bond angle modifications

As was done in our earlier study, it is of some interest to determine the effects of modified geometry on the calculated chemical shift. Shift derivatives were calculated both for bond length modifications (one heavy-atom-hydrogen bond modified) and for angle modifications (all angles simultaneously modified in the molecule) and the data is presented in Table IV. For the second-row hydrides studied here the primary 6-211G(2d) basis was employed; for comparison, results obtained previously on some first-row hydrides are also contained in Table IV where a 6-311G(d) basis was used.

As was noted earlier, the shift derivatives with respect to bond length modification are all negative for the heavy atoms involved as well as the bond-modified hydrogens ( $\sigma_{r(1)}$ ) and the bond-unmodified hydrogens ( $\sigma_{r(2)}$ ). In virtually all cases the shift derivatives are dominated by the paramagnetic term, the one exception being  $\text{SiH}_4$  where the overall bond length derivative is very small. Both for first- and second-row hydrides the heavy atom bond length derivatives are nearly linear in the chemical shift itself which is directly related to the position of the heavy atom in its row of the Periodic Table. The bond length derivatives for hydro-

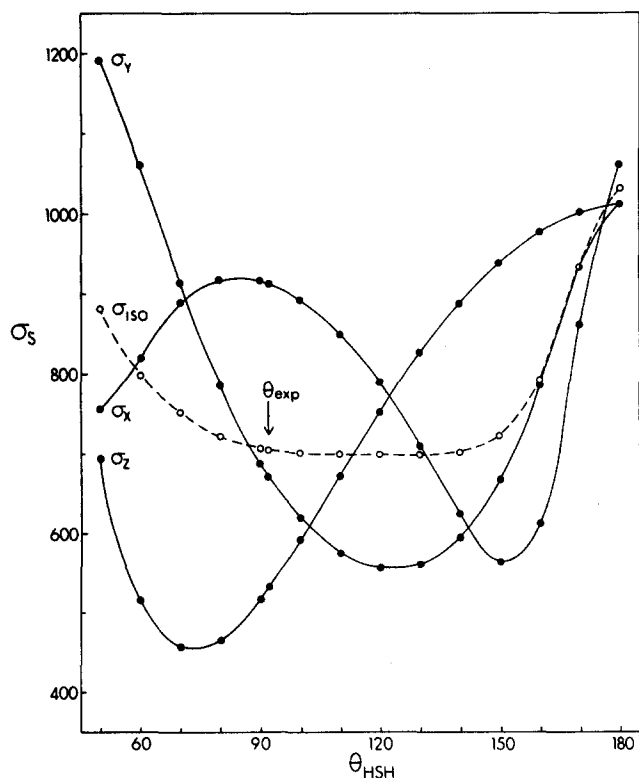


FIG. 3. Angular variation of the various shift components in  $\text{H}_2\text{S}$  as a function of the HSH angle. The HS bond length was optimized at each bond angle.

TABLE III. Heavy atom chemical shifts  $\sigma$ , shift anisotropies  $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ , hydrogen shifts, and molecular energies for some second-row hydrides. A resonant atom gauge origin for the heavy atoms is used by the other authors cited here.

	HL <sup>a</sup>	LZ <sup>b</sup>	KA <sup>c</sup>	Current work	Experiment
$\sigma$					
HCl	939.0	945.2		948.4	950 <sup>d</sup>
H <sub>2</sub> S	718.5	704.3		713.1	
PH <sub>3</sub>	584.9	577.6	589.6	598.1	594 <sup>d</sup>
SiH <sub>4</sub>	480.9	472.2		499.5	
$\Delta\sigma$					
HCl	314.9	305.7		301.4	298 <sup>d</sup>
H <sub>2</sub> S	31.39	325.3		301.6	
PH <sub>3</sub>	-36.4	-39.8	-38.8	-32.8	-52, <sup>d</sup> -55.5 <sup>e</sup>
$\sigma_H$					
HCl	29.25 <sup>f</sup>	30.70 <sup>g</sup>		31.68	
H <sub>2</sub> S	30.03	30.96		31.65	
PH <sub>3</sub>	28.73	30.16	32.07 <sup>h</sup>	30.24	
SiH <sub>4</sub>	27.96	28.08		28.62	
$E$					
HCl		-460.1016		-460.0624	
H <sub>2</sub> S		-398.7106		-398.6692	
PH <sub>3</sub>		-342.4860		-342.4485	
SiH <sub>4</sub>		-291.2613		-291.2247	

<sup>a</sup>Reference 5(b).

<sup>b</sup>Reference 21.

<sup>c</sup>Reference 25.

<sup>d</sup>Based on  $\sigma_{\text{para}}$  from the experimental work of Gierke and Flygare (Ref. 20), and  $\sigma_{\text{dia}}$  averaged from the theoretical calculations of HL and LZ [Refs. 5(b) and 21].

<sup>e</sup>Reference 22.

<sup>f</sup>Best origin for HL  $\sigma_H$  calculations.

<sup>g</sup>Center-of-mass origin for LZ  $\sigma_H$  calculations.

<sup>h</sup> $\sigma_H$  origin at H-atom.

TABLE IV. Bond length and bond angle chemical shift derivation data (ppm/Å or ppm/deg) for some first- and second-row hydrides. Hydrogen derivative shift data refers to the hydrogen in the length modified bond ( $\sigma'_{r(1)}$ ) and those attached by fixed bond lengths ( $\sigma'_{r(2)}$ ). For angle derivatives, all bond angles were simultaneously modified. Angle derivative data has been multiplied by 100 for ease of presentation.

(1) Bond length derivatives							
		Heavy atom			Hydrogen		
		$\sigma$	$\sigma'_r$	$0.5\sigma''_r$	$\sigma$	$\sigma'_{r(1)}$	$\sigma'_{r(2)}$
a.	CH <sub>4</sub>	193.0	-51.0	-70.1	31.85	-25.47	-2.60
	NH <sub>3</sub>	265.2	-129.2	-242.4	32.71	-31.67	-3.84
	H <sub>2</sub> O	332.0	-275.0	25.8	32.04	-36.09	-4.82
	HF	412.4	-444.0	-713.5	30.18	-42.16	...
b.	SiH <sub>4</sub>	499.5	-17.1	-113.4	28.62	-14.71	-1.08
	PH <sub>3</sub>	598.1	-148.4	-248.4	30.24	-19.60	-1.88
	H <sub>2</sub> S	713.1	-420.2	-622.9	31.65	-26.25	-3.49
	HCl	948.4	-682.4	-921.2	31.68	-34.10	...
(2) Bond angle derivatives							
		Heavy atom			Hydrogen		
		$\sigma$	$100\sigma'$	$0.5(100\sigma''_{\theta})$	$\sigma$	$100\sigma'$	$0.5(100\sigma''_{\theta})$
a.	NH <sub>3</sub>	265.2	-28.3	6.2	32.71	-7.36	0.040
	H <sub>2</sub> O	332.0	-6.0	3.7	32.04	-5.76	0.063
b.	PH <sub>3</sub>	598.1	-596.3	13.3	30.24	-8.15	-0.073
	H <sub>2</sub> S	713.1	-104.1	5.2	31.65	-4.32	-0.076

gen also parallel the position of the heavy atom in its row but do not correlate linearly with the hydrogen chemical shift itself. The shift derivatives of the heavy atoms in both rows are comparable as are the two sets of the bond-modified hydrogens; the shift derivatives for those hydrogens on bonds where the length was not changed in the derivative calculation again are comparable for the two rows but are an order of magnitude smaller than the derivatives for hydrogens directly involved in the modified bond.

Symmetrically changing the bond angles in the hydrides results in the angle derivative data seen in part 2 of the table. Several differences are to be noted in the angle derivative data compared to the bond length derivatives. Here the second derivatives with regard to angle are much smaller than the first derivatives both for the heavy atoms and the hydrogens. Secondly, the second-row atoms are much more sensitive with regard to a bond angle change than are their counterparts in the first row. For example,  $\text{PH}_3$  decreases by approximately 6.0 ppm for an increase of  $1^\circ$  in the HPH bond angles while for  $\text{NH}_3$  a  $1^\circ$  increase in bond angle results in a decrease of just 0.3 ppm. If we contrast the shifts per degree of angle change with those calculated for a bond length angle change of  $0.01 \text{ \AA}$  one can see that bond length changes of this magnitude have a larger effect on the chemical shift than a degree change in angle for the first-row hydrides; this role is modified for the second-row hydrides where the calculated change in the chemical shift per degree of bond angle is comparable to that predicted per  $0.01 \text{ \AA}$  of bond length. It would be of considerable interest to see if this relationship obtains for these atoms in larger molecules.

## SUMMARY

The triple-split-valence basis with two sets of  $d$  polarization functions in the GIAO SCF approach is an efficient basis for the calculation of reasonably accurate chemical shift effects in  $\text{PH}_3$ . In  $\text{PH}_3$  the use of  $sp$ -diffuse functions has little effect near the equilibrium geometry and they are not used in the primary basis; however, for the planar case they have a noticeable effect. Generally speaking, optimized geometries should be employed when investigating nonequilib-

rium structures since bond modification effects can be sizable for atoms in the second row. Shift surfaces for the various shift components are generally more complicated than that of the isotropic chemical shift; a thorough understanding of the various contributions to the chemical shift from the individual components will likely be required for a fundamental understanding of the shift and shift anisotropies.

<sup>1</sup>Numbers in parentheses indicate the contraction of the Gaussian orbitals for  $s, p, d, \dots$  functions, in that order. Square bracket notations indicate the actual number of atomic orbitals of the indicated type.

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