

## Second-Row Molecular Orbital Calculations. 5. A Minimal Basis INDO for Na-Cl

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**Abstract:** An INDO method is developed for molecules containing Na-Cl. Using only valence s and p orbitals, the parametrization is carried out in the spirit of the approach originally taken by Pople and co-workers. The reliability of the method is tested by calculating geometries, dipole moments, and internal rotation barriers for approximately 100 molecules. The improvement in predictive ability relative to previous parametrizations is considerable. Predicted geometries are nearly as good as those for STO3G. Dipole moments of molecules containing Si and Cl are in excellent agreement with experiment, while for P and S the agreement is only fair.

### I. Introduction

The aim of this series of papers<sup>1-4</sup> is to develop a semiempirical INDO parametrization for the second row of the periodic table (Na-Cl). To the extent that it is possible, the intent is to maintain consistency with the methodology and level of accuracy of the original CNDO/2<sup>5</sup> and INDO<sup>6</sup> parametrizations for the first row. As a first step in this direction, four of the more popular second-row parametrizations were critically surveyed to test their ability to reproduce experimental dipole moments<sup>2</sup> and geometries.<sup>3</sup> The results of these surveys were disappointing since none of the methods investigated are able to consistently reproduce trends or magnitudes for these properties. In particular, the level of accuracy is considerably lower than that for the first-row methods.<sup>7,8</sup>

Among the numerous reasons for the failure of these second-row methods, the most plausible seem to be (1) the use of inappropriate orbital exponents; (2) inadequate parametrization; (3) an inability of minimal or minimal +3d basis sets to consistently reproduce experimental properties for second-row molecules; (4) a basic failure of the INDO (or CNDO) methodology, at least within the original framework of these methods.

In order to at least partially answer reasons (1) and (3) a set of diatomic molecules was studied in part 4 using minimal and minimal +3d Slater basis sets.<sup>4</sup> The molecules were chosen to span as wide a range of environments as possible for each second-row atom, and the valence orbital exponents were varied (a) for a minimal 3sp basis, (b) for a 3spd basis keeping all  $n = 3$  exponents equal for each atom, and (c) for a 3spd basis allowing separate d orbital exponents. While the predicted bond lengths and dipole moments are not perfect, the important results of this study are that molecule-optimized exponents significantly improve agreement with experiment and that the ab initio results are considerably more accurate than the semiempirical methods tested earlier. Further evidence that this level of nonempirical calculation can provide reasonable results is given by the recent STO3G and STO3G\* geometry survey for second-row molecules.<sup>9</sup>

While reason (4) cannot be discounted, all of the existing methods suffer from inadequate parametrization in addition to the choice of standard Slater exponents. Since this has been discussed in detail elsewhere,<sup>2</sup> suffice it to say that at the time of the original second-row parametrization by Santry and Segal<sup>10</sup> there were virtually no nonempirical calculations to use for reference. The calculations presented in part 4<sup>4</sup> now provide a consistent set of reference calculations which may be used to determine semiempirical parameters.

There has been considerable discussion over the years with regard to the role played by d orbitals in the chemistry of

molecules containing second-row atoms.<sup>11</sup> Indeed, there are clearly systems for which the inclusion of d orbitals is expected to have a qualitative effect on predicted results. Nonetheless, in general it is not clear whether observed improvements in predicted results upon addition of d orbitals to a minimal basis set is due to the inherent nature of d orbitals or to an inadequate choice of the minimal basis functions. In part 4, for example, it was found that a minimal basis set with optimized valence exponents provided agreement with experiment equivalent to that using an spd basis with Slater exponents. For a semiempirical method one might expect this problem to be magnified due to the tendency to overemphasize the role of d orbitals.<sup>2</sup> Furthermore, the addition of d functions to the INDO basis results in a significant increase in the time required for the calculation, particularly if the molecule contains many second-row atoms.

For these reasons our approach for developing modified and, hopefully, improved versions of INDO for the second row will be a two-step process. In the first step, presented here, an optimal set of parameters is obtained for a minimal valence basis set containing only s and p functions. The parametrization for a d-orbital-containing method is currently underway and will be presented in a later paper.

### II. Parametrization

The four sets of parameters needed for INDO<sup>6</sup> are the orbital exponents ( $\zeta_A$ ), the Slater-Condon factors ( $F_A^2$ ,  $G_A^1$ ), the resonance or binding parameters ( $\beta_A^0$ ), and the Mulliken electronegativities  $-\frac{1}{2}(I + A)\mu$ , where  $\mu$  is s or p. The final values for each set are listed in Table I. Except for a slightly modified value for Na, the exponents are those presented previously.

The Slater-Condon factors were determined in a manner analogous to that suggested by Stevenson.<sup>12</sup> If  $X^{(1)}$  and  $X^{(2)}$  represent a Slater-Condon factor ( $X = F^2$  or  $G^1$ ) for an element in a given group of row 1 and row 2, respectively, then

$$X_{\text{expt}}^{(2)} = \frac{X_{\text{calcd}}^{(2)}}{X_{\text{calcd}}^{(1)}} X_{\text{expt}}^{(1)} \quad (1)$$

In eq 1  $X_{\text{calcd}}^{(i)}$  represents the calculated factor, while  $X_{\text{expt}}^{(1)}$  refers to the set of Slater-Condon factors used by Pople and co-workers<sup>6</sup> for the first row. In this way one can obtain a set of "experimental" Slater-Condon factors for the second row. The values presented in Table I are slightly different from those quoted by Stevenson owing to the difference in orbital exponents.

With the first two sets of parameters fixed as described above, the electronegativity parameters were initially set equal to the original Santry-Segal values<sup>10</sup> in order to determine an

Table I. INDO Parameters

	Na	Mg	Al	Si	P	S	Cl
$\zeta_A$	1.21	1.28	1.39	1.55	1.74	1.93	2.14
$F_{A_s}^2$ , au	0.071 957	0.090 701	0.108 090	0.128 450	0.151 521	0.175 202	0.201 492
$G_{A_s}^1$ , au	0.128 648	0.138 735	0.160 025	0.191 790	0.231 907	0.276 683	0.329 070
$-\beta_{A_s}^0$ , eV	4.0	7.0	9.0	8.0	13.0	16.5	18.0
$-\frac{1}{2}(I + A)_s$ , eV	2.804	5.125	7.771	7.50	16.20	17.51	25.11
$-\frac{1}{2}(I + A)_p$ , eV	1.302	2.052	2.995	4.00	4.10	3.45	6.34

Table II. Diatomic Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	STO3G <sup>c</sup>	BH <sup>d</sup>
Na <sub>2</sub>	3.078	1.860		
Mg <sub>2</sub>	2.228	1.800		
Al <sub>2</sub> <sup>d</sup>	2.560	1.968		
Si <sub>2</sub>	2.252	1.925		2.088
P <sub>2</sub>	1.894	1.848	1.808	2.037
S <sub>2</sub> <sup>e</sup>	1.889	1.862		2.039
Cl <sub>2</sub>	1.988	1.902	2.063	2.061
NaH	1.887	1.373	1.654	
AlH	1.646	1.515		
PH <sup>e</sup>	1.432	1.426		1.514
HCl	1.27	1.325	1.313	1.396
NaF	1.931	1.663		
AlF	1.654	1.840	1.616	
ClF	1.628	1.547	1.677	1.618
SiO	1.509	1.645		1.808
LiCl	2.020	2.197		2.309
BCl	1.715	1.640		1.734
CS	1.535	1.494		1.591
PN	1.491	1.519		1.623
NaCl	2.361	1.867	2.221	
AlCl	2.130	2.050	2.164	
SiS	1.928	1.899		2.136

<sup>a</sup> Bond lengths in Å. <sup>b</sup> G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. I, Van Nostrand, Princeton, N.J., 1950. <sup>c</sup> Reference 9. <sup>d</sup> Reference 3. <sup>e</sup> Triplet ground state.

initial set of  $\beta_A^0$ . The procedure used is similar to that described by Pople and Segal.<sup>5</sup> For each second-row atom three diatomic molecules (the homonuclear, the hydride, and the oxide or fluoride) were chosen as reference systems, with the bond lengths at their experimental values. For each molecule,  $\beta_A^0$  for the second-row atom was varied and the following function minimized:

$$f_1 = \sum_i^{\text{occ}} [C_{\mu i}^a - C_{\mu i}^I]^2 \quad (2)$$

where the  $C_{\mu i}$  are occupied LCAO MO coefficients and the superscripts a and I refer to ab initio and INDO wave functions, respectively. In order to have a valid comparison the ab initio MOs were first transformed to a Löwdin orthogonal basis.<sup>13</sup> Typically, the minimum in  $f_1$ , for a given atom A, does not occur at the same value of  $\beta_A^0$  for all three reference molecules. Thus, a "best" value was chosen by comparing the three curves and by taking eigenvalue differences, virtual orbital coefficients, and orbital ordering into account for fine tuning. At this point in the parametrization optimal geometries were calculated for a representative subset of small molecules.

Using the previously determined set of  $\beta_A^0$ , the electronegativity parameters for Si-Cl were adjusted by minimizing the function  $f_2$  for a set of 25 molecules:

$$f_2 = \sum_{i=1}^{25} [(\mu_i^{\text{expt}} - \mu_i^{\text{calcd}}) / \mu_i^{\text{expt}}]^2 \quad (3)$$

where  $\mu_i$  refers to the magnitude of the dipole moments. This function was chosen in preference to a simple minimization of

Table III. AX<sub>2</sub> Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	STO3G <sup>c</sup>	BH <sup>d</sup>
AlH <sub>2</sub>	1.59	1.49		
	119.0	119.9		
PH <sub>2</sub>	1.428	1.42		1.51
	91.5	94.0		97.87
SH <sub>2</sub>	1.328	1.36	1.329	1.44
	92.2	94.3	92.53	98.48
SiF <sub>2</sub>	1.591	1.79		1.99
	101.0	96.2		94.25
MgF <sub>2</sub> <sup>e</sup>	1.770	1.82	1.665	
	180.0	180.0	180.0	
SCl <sub>2</sub>	2.00	1.95		2.12
	103.0	100.7		100.64
CS <sub>2</sub>	1.554	1.55		1.63
	180.0	180.0		180.0
SO <sub>2</sub>	1.432	1.56	1.562	1.67
	119.536	106.6	109.19	106.51
ClO <sub>2</sub>	1.473	1.55		1.66
	117.6	105.9		106.0

<sup>a</sup> Bond lengths in Å, angles in degrees. For each molecule geometric parameters are given in the order bond length, angle. <sup>b</sup> G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966, unless otherwise noted. <sup>c</sup> Reference 9. <sup>d</sup> Reference 3. <sup>e</sup> P. A. Akishin and M. Spiridonov, *Sov. Phys.-Crystallogr. (Engl. Transl.)*, **12**, 472 (1957).

absolute errors in order to obtain a consistent percentage deviation from experiment; however, the minima in the absolute deviations were found to occur at essentially the same values of  $-\frac{1}{2}(I + A)_\mu$  as the minima in  $f_2$ . It should be noted that this procedure did not work well for Si. For this atom the  $f_2$  dependence on  $-\frac{1}{2}(I + A)_s$  is extremely flat, with a slight downward slope toward a value of  $-\frac{1}{2}(I + A)_s = 0$ . This is clearly inappropriate and results in orbital orderings which, to say the least, are difficult to rationalize. Thus, for Si a "realistic" set of  $-\frac{1}{2}(I + A)_\mu$  have been chosen, for which  $f_2$  is close to the minimum value and considerably lower than that for the original parameters. For Na, Mg, and Al this procedure was not followed owing to a lack of experimental dipole moments, and the electronegativity parameters used are those originally determined by Santry and Segal.<sup>10</sup>

The final step in the parametrization was to reoptimize the geometries for the small subset of molecules. Since no significant changes were found in these geometries, relative to those obtained prior to optimization of  $f_2$ , further adjustment of the  $\beta_A^0$  was deemed unnecessary.

Finally, it is useful to note that for all but two (Na<sub>2</sub> and Cl<sub>2</sub>) of the reference diatomic molecules the ab initio valence orbital ordering is faithfully reproduced by INDO. In Na<sub>2</sub> the virtual  $2\sigma_g$  and  $1\pi_g$  MOs are reversed, while in Cl<sub>2</sub> the occupied  $1\pi_g$  and  $2\sigma_g$  MOs are reversed.

### III. Geometries

Geometry optimizations have been carried out on a number of small to moderate size molecules using the gradient method of McIver and Komornicki,<sup>14</sup> extended to include 3s and 3p

Table IV. XAY Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	STO3G <sup>c</sup>	BH <sup>d</sup>
HCCl	1.12	1.13		1.12
	1.68	1.61		1.69
HSiCl	103.4	107.6		106.31
	1.561	1.51		1.61
OCS	2.064	2.07		2.33
	102.8	100.8		97.03
HCP	1.160	1.24		1.22
	1.560	1.54		1.65
HPO	180.0	180.0		180.0
	1.067	1.10		1.10
CICN <sup>e</sup>	1.542	1.51	1.471	1.60
	180.0	180.0	180.0	180.0
HPO	1.433	1.44		1.52
	1.512	1.60		1.72
HCP	104.7	100.7		101.40
	1.629	1.64		1.71
HPO	1.160	1.19		1.18
	180.0	180.0		180.0

<sup>a</sup> Bond lengths in Å, angles in degrees. Geometric parameters listed in the order  $R_{AX}$ ,  $R_{AY}$ , XAY angle. <sup>b</sup> G. Herzberg, "Electronic Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966, unless otherwise noted. <sup>c</sup> Reference 9. <sup>d</sup> Reference 3. <sup>e</sup> W. J. Lafferty, D. R. Lide, and R. A. Toth, *J. Chem. Phys.*, **43**, 2063 (1965).

Table V. AX<sub>3</sub> Molecules<sup>a</sup>

Molecule	Expt	INDO	STO3G <sup>b</sup>	BH <sup>c</sup>
PH <sub>3</sub> <sup>d</sup>	1.412	1.42	1.378	1.51
	93.36	94.0	95.01	97.88
PF <sub>3</sub> <sup>e</sup>	1.570	1.70		1.83
	97.8	95.5		95.87
PCl <sub>3</sub> <sup>f</sup>	2.039	2.03		2.22
	100.27	99.5		98.97
SO <sub>3</sub> <sup>g</sup>	1.4198	1.57		1.67
	120.0	120.0		120.0
BCl <sub>3</sub> <sup>h</sup>	1.742	1.74		1.80
	120.0	120.0		120.0
AlCl <sub>3</sub> <sup>i</sup>	2.06	2.10		
	120.0	120.0		
AlF <sub>3</sub> <sup>j</sup>	1.63	1.84	1.560	
	120.0	120.0	120.0	

<sup>a</sup> Bond lengths in Å, angles in degrees. Geometric parameters listed in the order  $R_{AX}$ , XAX angle. <sup>b</sup> Reference 9. <sup>c</sup> Reference 3. <sup>d</sup> F. Y. Chu and T. Oka, *J. Chem. Phys.*, **60**, 4612 (1974). <sup>e</sup> Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969). <sup>f</sup> K. Hedberg and M. Iwasaki, *J. Chem. Phys.*, **36**, 589 (1962). <sup>g</sup> A. Kaldor, *J. Mol. Struct.*, **15**, 123 (1973). <sup>h</sup> S. Konaka, Y. Murata, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **39**, 1134 (1966). <sup>i</sup> E. Z. Zasorin and N. S. Rambidi, *J. Struct. Chem. (Engl. Transl.)*, **8**, 347 (1967). <sup>j</sup> G. Shanmugasundaram and G. Nagarajan, *Z. Phys. Chem. (Leipzig)*, **240**, 363 (1969).

functions. The results are compared with the experimental geometries in Tables II–X. Also listed in these tables are geometries predicted earlier<sup>3</sup> using the Benson and Hudson (BH) version of INDO<sup>15</sup> and using STO3G.<sup>9</sup> Since the earlier INDO method was not parametrized for Na–Al and since the number of small molecules containing these atoms is small, the following discussion is split into two parts, the first dealing with molecules containing Si–Cl and the second with molecules containing Na, Mg, or Al.

**A. Si–Cl.** The most striking failure of methods considered in part 3 was the inability to reproduce bond lengths connecting a second-row atom with N, O, or F. Such bond lengths were generally overestimated by 0.2–0.5 Å. Similar, but not as drastic, problems were encountered for A–Cl bonds when A

Table VI. AX<sub>2</sub>Y and AX–BY Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	STO3G <sup>c</sup>	BH <sup>d</sup>
NH <sub>2</sub> Cl <sup>e</sup>	1.014	1.07		1.07
	1.770	1.62		1.70
SOF <sub>2</sub>	106.8	104.4		104.83
	102.0	107.6		106.05
SOCl <sub>2</sub> <sup>f</sup>	1.585	1.62		1.71
	1.412	1.58		1.73
SOCl <sub>2</sub> <sup>f</sup>	92.8	95.5		95.63
	106.8	102.6		103.63
F <sub>2</sub> CS <sup>g</sup>	2.076	1.96		2.14
	1.443	1.60		1.74
Cl <sub>2</sub> CS	96.1	99.6		104.35
	106.3	103.8		99.24
Cl <sub>2</sub> CS	1.315	1.34		1.32
	1.589	1.58		1.67
Cl <sub>2</sub> CS	107.1	104.6		105.58
	126.45	127.7		127.21
Cl <sub>2</sub> CS	1.70	1.68		1.73
	1.63	1.58		1.67
Cl <sub>2</sub> CO	116.0	110.3		111.26
	122.0	124.8		124.37
Cl <sub>2</sub> CO	1.75	1.67		1.74
	1.17	1.26		1.25
PFC <sub>2</sub>	111.30	115.4		113.40
	124.35	122.3		123.30
PFC <sub>2</sub>	2.02	2.02		2.22
	1.55	1.72		1.84
ClF <sub>3</sub>	102	99.8		99.19
	102	97.3		97.50
ClF <sub>3</sub>	1.698	1.60	1.791	1.68
	1.598	1.56	1.787	1.65
HCNS	185.0	169.8		199.78
	87.5	84.9	77.8	80.11
HCCCl <sup>h</sup>	1.22	1.25		1.21
	1.01	1.06		1.05
HCCCl <sup>h</sup>	1.56	1.56		1.68
	130.25	130.9		180.0
HCCCl <sup>h</sup>	180.0	171.4		180.0
	1.204	1.20		1.20
HCCCl <sup>h</sup>	1.055	1.09		1.09
	1.637	1.65		1.71
HCCCl <sup>h</sup>	180.0	180.0		180.0
	180.0	180.0		180.0

<sup>a</sup> Order of geometric parameters for AX<sub>2</sub>Y molecules is  $R_{AX}$ ,  $R_{AY}$ , XAX angle, XAY angle. For AX–BY molecules the order is  $R_{AB}$ ,  $R_{AX}$ ,  $R_{BY}$ , XAB angle, ABY angle. <sup>b</sup> L. E. Sutton, "Tables of Interatomic Distances", The Chemical Society, London, 1958, unless otherwise noted. <sup>c</sup> Reference 9. <sup>d</sup> Reference 3. <sup>e</sup> G. D. Bendazoli, D. G. Lister, and P. Palmieri, *J. Chem. Soc., Faraday Trans. 2*, **69**, 791 (1973). <sup>f</sup> I. Hargittai, *Acta Chim. Acad. Sci. Hung.*, **60**, 231 (1969). <sup>g</sup> A. J. Careless, H. W. Kroto, and B. M. Landsberg, *Chem. Phys.*, **1**, 371 (1973). <sup>h</sup> J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.*, **59**, 2661 (1963).

is a second-row atom. Neither of these problems was encountered for the minimal basis calculations on diatomics, and perusal of the tables indicates that STO3G handles such bond lengths reasonably well. Thus, the ability of the reparametrized INDO to treat these two types of bonds is an important test of the method. While A–X bonds are still predicted to be too long, particularly for X = F, O, the improvement relative to previous methods is considerable. This comparison is summarized in Table XI, where the average absolute errors in A–X bond lengths are listed for INDO, BH, and SPD'. The latter method is a reparametrization of CNDO developed by Santry.<sup>16</sup> The SPD' results are included in the table since this method was judged to be the most reliable of previously tested parametrizations.<sup>3</sup>

The improvement in bond length predictions is seen to be most striking for A–F, A–O, and A–Cl bonds, with the present

Table VII. AX<sub>4</sub> Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	STO3G <sup>c</sup>	BH <sup>d</sup>
SiH <sub>4</sub>	1.480	1.48	1.421	1.59
SiF <sub>4</sub> <sup>e</sup>	1.555	1.79		1.98
SiCl <sub>4</sub>	2.01	2.11		2.34
CCl <sub>4</sub>	1.766	1.70		1.76

<sup>a</sup> Bond lengths in Å. <sup>b</sup> L. E. Sutton, "Tables of Interatomic Distances", The Chemical Society, London, 1958, unless otherwise noted. <sup>c</sup> Reference 9. <sup>d</sup> Reference 3. <sup>e</sup> B. Beagley, D. P. Brown, and J. M. Freeman, *J. Mol. Struct.*, **18**, 337 (1973).

Table VIII. AX<sub>3</sub>Y Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	STO3G <sup>c</sup>	BH <sup>d</sup>
SiH <sub>3</sub> F <sup>e</sup>	1.486	1.48	1.422	1.59
	1.593	1.81	1.624	2.01
	110.4	108.2	109.60	106.48
SiF <sub>3</sub> H	1.565	1.79		1.98
	1.455	1.47		1.58
	110.62	112.6		113.54
SiH <sub>3</sub> Cl	1.483	1.48		1.59
	2.048	2.11		2.35
	108.73	109.5		107.83
SiCl <sub>3</sub> H	2.021	2.11		2.34
	1.470	1.49		1.59
	109.54	109.7		110.88
SiF <sub>3</sub> Cl	1.56	1.80		1.98
	1.989	2.08		2.32
	110.42	112.0		110.94
CH <sub>3</sub> Cl	1.11	1.12		1.12
	1.78	1.68	1.802	1.75
	108.42	110.6		109.43
CCl <sub>3</sub> H	1.767	1.69		1.75
	1.073	1.13		1.12
	108.53	107.9		108.52
CF <sub>3</sub> Cl	1.328	1.34		1.34
	1.751	1.68		1.76
	110.9	112.2		111.44
CCl <sub>3</sub> F	1.76	1.69		1.76
	1.40	1.36		1.34
	107.36	107.3		108.29
PF <sub>3</sub> O	1.524	1.69	1.612	1.82
	1.436	1.70	1.557	1.86
	115.10	119.1	116.76	118.96
PF <sub>3</sub> S	1.53	1.70		1.83
	1.86	2.01		2.26
	117.56	120.8		119.84
PCl <sub>3</sub> S <sup>f</sup>	2.011	2.04		2.23
	1.885	2.02		2.24
	116.35	117.2		116.79

<sup>a</sup> Geometric parameters listed in the order R<sub>AX</sub>, R<sub>AY</sub>, XAY angle. <sup>b</sup> L. E. Sutton, "Tables of Interatomic Distances", The Chemical Society, London, 1958, unless otherwise noted. <sup>c</sup> Reference 9. <sup>d</sup> Reference 3. <sup>e</sup> R. Kewley, P. M. McKinney, and A. G. Robiette, *J. Mol. Spectrosc.*, **1**, 243 (1973). <sup>f</sup> T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971).

version being on the order of 0.1 Å closer to experiment. In particular, A-cl bonds are now handled quite well. Also included in Table XI are average absolute errors for A-H bonds. These are now in excellent agreement with experiment with an average absolute error a factor of 5 smaller than that for previous methods.

With regard to specific molecules, the following points are noteworthy. Except for Si<sub>2</sub>, homonuclear diatomic bond lengths are handled reasonably well (Table II). The observed decrease from Si<sub>2</sub> to S<sub>2</sub> and subsequent increase in the Cl<sub>2</sub> bond length are reproduced. While the bond in Si<sub>2</sub> is predicted to be way too short, this does not appear to carry over to poly-

Table IX. AX<sub>2</sub>Y<sub>2</sub> Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	BH <sup>c</sup>
CCl <sub>2</sub> H <sub>2</sub>	1.772	1.69	1.75
	1.068	1.12	1.12
	111.80	112.6	109.00
	108.27	109.2	111.29
CF <sub>2</sub> Cl <sub>2</sub>	1.35	1.35	1.34
	1.74	1.69	1.76
	109.0	104.65	105.75
	108.69	109.34	109.72
SO <sub>2</sub> F <sub>2</sub> <sup>d</sup>	1.405	1.59	1.74
	1.530	1.61	1.71
	123.97	127.9	128.76
	108.12	107.2	106.87
SO <sub>2</sub> Cl <sub>2</sub> <sup>e</sup>	1.404	1.61	1.75
	2.011	1.96	2.14
	123.5	122.0	123.65
	107.7	108.0	107.68
F <sub>2</sub> 'SF <sub>2</sub> <sup>f</sup>	1.545	1.62	1.74
	1.646	1.65	1.74
	101.5	108.3	135.71
	87.78	83.9	81.84

<sup>a</sup> Geometric parameters listed in the order R<sub>AX</sub>, R<sub>AY</sub>, XAX angle, XAY angle. <sup>b</sup> L. E. Sutton, "Tables of Interatomic Distances", The Chemical Society, London, 1958, unless otherwise noted. <sup>c</sup> Reference 3. <sup>d</sup> D. R. Lide, D. E. Mann, and J. J. Comeford, *Spectrochim. Acta*, **21**, 497 (1965). <sup>e</sup> I. Targittai, *Acta Chim. Acad. Sci. Hung.*, **60**, 231 (1969). <sup>f</sup> W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962).

Table X. AX<sub>2</sub>YZ Molecules<sup>a</sup>

Molecule	Expt <sup>b</sup>	INDO	BH <sup>c</sup>
CH <sub>2</sub> FCI	1.078	1.12	1.12
	1.378	1.35	1.34
	1.76	1.68	1.76
	111.9	108.7	110.01
	109.53	108.3	109.16
	109.1	111.1	109.64
CF <sub>2</sub> HCl	1.36	1.35	1.34
	1.06	1.13	1.12
	1.73	1.68	1.76
	110.5	105.2	105.80
		109.4	110.22
	110.5	110.2	109.93
CCl <sub>2</sub> HF	1.73	1.69	1.76
	1.06	1.13	1.12
	1.41	1.35	1.34
	112.	113.0	111.40
		109.8	109.39
	109.	108.3	108.75

<sup>a</sup> Geometric parameters listed in the order R<sub>AX</sub>, R<sub>AY</sub>, R<sub>AZ</sub>, XAX angle, XAY angle, XAZ angle. <sup>b</sup> L. E. Sutton, "Tables of Interatomic Distances", The Chemical Society, London, 1958. <sup>c</sup> Reference 3.

atomic molecules since the predicted geometry for disilane (see section IV) is in reasonable agreement with experiment.

Generally, the bond angles for AX<sub>2</sub> molecules are predicted reasonably well, with the observed decrease from water<sup>8</sup> to hydrogen sulfide reproduced correctly. An exception to this good agreement is SO<sub>2</sub>, for which the angle is predicted to be 13° too small. A similar problem was encountered for STO3G,<sup>9</sup> and Pople et al. concluded that d orbitals are necessary to reproduce the experimental angle. In Table V the angle in phosphine is properly predicted to be more than 10° smaller than in ammonia,<sup>8</sup> and the steady increase in bond angle from PH<sub>3</sub> to PF<sub>3</sub> to PCl<sub>3</sub> is reproduced. The latter trend was not reproduced by previous methods.<sup>6</sup> While PF and SO bond lengths are too long, they are much improved relative to

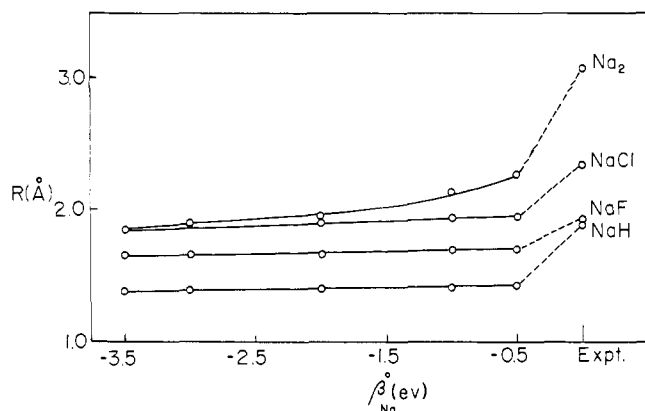


Figure 1. Na bond lengths vs.  $\beta_{\text{Na}}^{\circ}$  ( $\zeta = 1.21$ ).

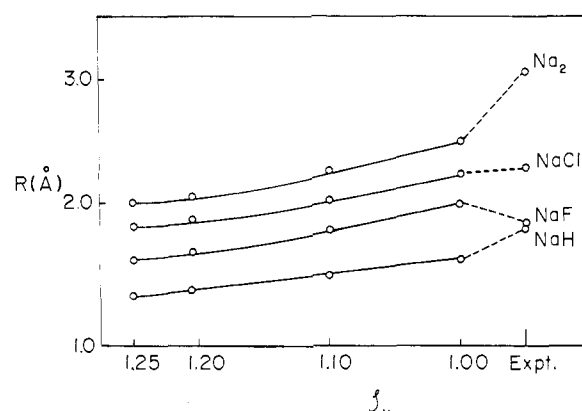


Figure 2. Na bond lengths vs.  $\zeta_{\text{Na}}$  ( $\beta_{\text{Na}}^{\circ} = -1.0$  eV).

Table XI. Average Absolute Errors in A-X Bonds<sup>a</sup> (Å)

Bond type	INDO	BH <sup>b</sup>	SPD' <sup>b</sup>	Sample size
A-F	0.143	0.243	0.224	16
A-O	0.146	0.290	0.230	10
A-N	0.089	0.101	0.101	2
A-Cl	0.057	0.211	0.149	12
A-H	0.018	0.100	0.094	12

<sup>a</sup> A = Si, P, S, Cl. <sup>b</sup> Reference 3.

Table XII. Error Analysis for Si-Cl

	BH	SPD'	STO3G	INDO	Sample size <sup>a</sup>
I. R	0.147	0.115	0.058	0.068	24 <sup>b</sup>
$\alpha$	6.49	3.94	2.81	2.55	11 <sup>c</sup>
II. R	0.170	0.141		0.082	87 <sup>d</sup>
$\alpha$	4.98	3.79		2.73	57 <sup>e</sup>

<sup>a</sup> Obvious values (e.g., tetrahedral for AX<sub>4</sub>, 120 for BCl<sub>3</sub>) are not included. <sup>b</sup> For BH sample size = 16. <sup>c</sup> For BH sample size = 6. <sup>d</sup> For BH sample size = 79. <sup>e</sup> For BH sample size = 51.

earlier parametrizations. The XAX angle increase from SOF<sub>2</sub> to SOCl<sub>2</sub> and from F<sub>2</sub>CS to Cl<sub>2</sub>CS is reproduced correctly (Table VI); however, the Cl-C-Cl angle in Cl<sub>2</sub>CO is incorrectly predicted to be larger than that in Cl<sub>2</sub>CS. Consistent with the general decrease in predicted bond lengths, C-Cl bonds are now predicted to be somewhat too short (Tables VI-X).

The overall quality of predicted geometries for bonds and angles containing Si-Cl is summarized in the error analysis in Table XII. Two sets of average absolute errors are given in this table. In the first set (I) only those molecules are included for which STO3G results are available. This set includes the four molecules discussed in the following section. In the second set (II) all molecules excluding those containing Na, Mg, or Al are included. For set I the improvement relative to previous methods is obvious, and, in fact, the present method appears to compare favorably with STO3G. This latter point is somewhat misleading, however, since many of the A-X bond lengths which are predicted to be too long by INDO have not been treated by STO3G. This is reflected in the increase in the average bond length error for set II relative to set I. The improvement in predicted angles is also noticeable, particularly relative to BH.

In summary, the ability of the newly parametrized INDO to predict geometries for molecules containing Si-Cl is now comparable to the predictive ability of the same method for the first row.<sup>6</sup> The improvement relative to SPD' is particularly gratifying since it was pointed out earlier that a properly chosen set of parameters may be as important as the addition of d orbitals to the basis set.<sup>3</sup> Further, since BH INDO is an SP-only version of SPD', it is expected that addition of d orbitals to the present method may improve the results further.

**B. Na-Al.** The bond lengths predicted for molecules containing the first three atoms in the second row are significantly worse than those discussed above. This is particularly true for Na, for which all bonds are predicted to be far too short. The homonuclear bonds in Mg<sub>2</sub> and Al<sub>2</sub> are also predicted to be too short (Table II), and while the AlH bonds in AlH and AlH<sub>2</sub> are in successively better agreement with experiment, they are

also found to be short. As expected, the AlF bonds in AlF (Table II) and AlF<sub>3</sub> (Table V) are too long; however, the AlCl bonds in AlCl and AlCl<sub>3</sub> and the MgF bond in MgF<sub>2</sub> are reasonable.

Of the three atoms, Na is the most amenable to improvement since all of its bonds are predicted to be too short. Apparently this means that choosing an ab initio-optimized valence exponent and a "resonance" parameter fitted to ab initio results is inappropriate for this atom. These two parameters,  $\beta_{\text{Na}}^{\circ}$  and  $\zeta_{\text{Na}}$ , were reinvestigated in two steps. First,  $\beta_{\text{Na}}^{\circ}$  was varied, and the bond lengths for Na<sub>2</sub>, NaH, NaF, and NaCl were reoptimized, for  $\zeta_{\text{Na}}$  fixed at 1.21. As is apparent in Figure 1, all four bond lengths remain too small, even if  $\beta_{\text{Na}}^{\circ}$  is increased to -0.5 eV. Fixing  $\beta_{\text{Na}}^{\circ}$  at -1.0 eV and varying the exponent proved more fruitful (Figure 2). At an exponent of 1.0  $R(\text{Na}_2)$  and  $R(\text{NaH})$  are still too small, but the NaCl bond length is close to experiment and that for NaF is somewhat long. Further refinement is certainly possible; however, the results for  $\beta_{\text{Na}}^{\circ} = -1.0$  eV and  $\zeta = 1.0$  are probably close to optimal for this set of molecules and are comparable in accuracy to the predicted bond lengths using a minimal basis set ab initio technique.<sup>4</sup>

#### IV. Internal Rotation Barriers

The barriers to internal rotation in methylsilane, disilane, methylphosphine, and methyl mercaptan were calculated by optimizing the geometries of the eclipsed and staggered rotamers for each molecule. The resultant geometries are listed in Table XIII and the predicted barriers are compared with experiment and with other semiempirical results in Table XIV.

Aside from the fact that the C-S bond length in CH<sub>3</sub>SH is underestimated by 0.1 Å, the predicted geometries agree quite well with experiment. As was found for the analogous first-row molecules,<sup>1</sup> the effect of internal rotation on the various geometric parameters is generally small.

The barrier results are somewhat mixed. The decrease in barrier height from C<sub>2</sub>H<sub>6</sub> to Si<sub>2</sub>H<sub>6</sub> upon successive substitution

**Table XIII.** Geometries of CH<sub>3</sub>SiH<sub>3</sub>, Si<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>PH<sub>2</sub>, and CH<sub>3</sub>SH<sup>a</sup>

	CH <sub>3</sub> SiH <sub>3</sub>				Si <sub>2</sub> H <sub>6</sub>		
	S	E	Expt <sup>b</sup>		S	E	Expt <sup>c</sup>
C-Si	1.864	1.865	1.8668	Si-Si	2.272	2.273	2.327
C-H	1.120	1.120	1.093	Si-H	1.486	1.486	1.482
Si-H	1.487	1.487	1.485	HSiH	108.48	108.43	107.85
HCH	107.25	107.13	107.67				
HSiH	107.26	106.92	108.25				

	CH <sub>3</sub> PH <sub>2</sub>				CH <sub>3</sub> SH		
	S	E	Expt <sup>d</sup>		S	E	Expt <sup>e</sup>
C-P	1.792	1.794	1.863	C-S	1.716	1.718	1.819
C-Hi <sup>f</sup>	1.119	1.121	1.093	C-Hi <sup>f</sup>	1.122	1.120	1.093
C-Ho <sup>f</sup>	1.120	1.119		C-Ho <sup>f</sup>	1.123	1.123	
P-H	1.428	1.428	1.414	S-H	1.367	1.366	1.335
HCH	107.46	107.04	109.75	HCH	107.12	107.04	109.75
CPH	96.36	97.10	97.50	CSH	96.51	97.49	96.50
HPH	94.22	93.68	93.41				

<sup>a</sup> Bond lengths in Å, angles in degrees; S = staggered, E = eclipsed. <sup>b</sup> R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957). <sup>c</sup> K. C. Shatton, A. G. Lee, and W. J. Jones, *J. Raman Spectrosc.*, **1**, 243 (1973). <sup>d</sup> T. Kojima, E. L. Breig, and C. C. Lin, *J. Chem. Phys.*, **35**, 2139 (1961). <sup>e</sup> T. Kojima, *J. Phys. Soc. Jpn.*, **15**, 1284 (1960). <sup>f</sup> Hi and Ho refer to the in-plane and out-of-plane hydrogens, respectively.

**Table XIV.** Internal Rotation Barriers (kcal/mol)

Molecule	Expt	INDO	CNDO <sup>h</sup>	SPD' <sup>h</sup>	MBLD <sup>i</sup>
C <sub>2</sub> H <sub>6</sub>	2.875 <sup>a</sup>	2.25	2.25		
CH <sub>3</sub> SiH <sub>3</sub>	1.70 <sup>b</sup>	0.69	0.36	1.86	0.74
Si <sub>2</sub> H <sub>6</sub>	1.10 <sup>c</sup>	0.31	0.11	2.21	0.24
CH <sub>3</sub> NH <sub>2</sub>	1.97 <sup>d</sup>	1.91	2.07		
CH <sub>3</sub> PH <sub>2</sub>	1.96 <sup>e</sup>	1.32	0.79	1.78	0.85
CH <sub>3</sub> SH	1.27 <sup>f</sup>	1.12	0.71	1.04	0.73
CH <sub>3</sub> OH	1.07 <sup>g</sup>	1.21	1.25		

<sup>a</sup> W. J. Lafferty and E. K. Plyler, *J. Chem. Phys.*, **37**, 2688 (1962). <sup>b</sup> R. W. Kilb and L. Pierce, *ibid.*, **27**, 108 (1957). <sup>c</sup> R. A. Scott and H. A. Scheraga, *ibid.*, **42**, 2209 (1965). <sup>d</sup> T. Nishikawa, T. Itoh, and K. Shimada, *ibid.*, **23**, 1735 (1955). <sup>e</sup> T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961). <sup>f</sup> T. Kojima, *J. Phys. Soc. Jpn.*, **15**, 1284 (1960). <sup>g</sup> E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **21**, 1804 (1953). <sup>h</sup> Reference 1. <sup>i</sup> Barriers calculated at experimental geometries.

of Si for C is correctly reproduced. However, while all predicted barriers are improved relative to the earlier CNDO (SP)<sup>10</sup> results,<sup>1</sup> the values for CH<sub>3</sub>SiH<sub>3</sub> and Si<sub>2</sub>H<sub>6</sub> are still rather underestimated. For methylsilane, at least, this is not a result of using a minimal basis set since Ewig, Palke, and Kirtman<sup>17</sup> have recently calculated a 1.44 kcal/mol barrier for this molecule using a minimal STO basis. The poor barrier predictions for the two silicon compounds cannot be attributed to poor geometries, as was the case for CNDO (SP), in view of the results presented in Table XIII. A plausible explanation is that the long-range vicinal interactions, which are likely to play an important role in determining the barriers,<sup>18</sup> fall off too rapidly in the semiempirical method as the H...H distance is increased.

The predicted barriers for CH<sub>3</sub>PH<sub>2</sub> and CH<sub>3</sub>SH are in better agreement with experiment, although methylphosphine is incorrectly predicted to have a barrier height which is 0.6 kcal/mol smaller than methylamine. To investigate the possibility of a rapid decrease in vicinal H...H interactions as the cause for the small predicted barriers, these two barriers were recalculated at the experimental geometry. For both molecules this corresponds to an increase in the axial bond length and decreases the barriers to 0.85 and 0.73 kcal/mol, respectively.

As shown in Table XIV, addition of d orbitals increases the

**Table XV.** Dipole Moments for Molecules Containing Si or Cl (D)

Molecule <sup>a</sup>	Expt <sup>b</sup>	INDO	BH	SPD'
SiH <sub>3</sub> F*	1.268	1.21	1.25	0.28
CH <sub>3</sub> Cl*	1.94	1.41	2.19	1.76
SiH <sub>3</sub> Cl*	1.303	1.32	2.35	0.21
SiF <sub>3</sub> H*	1.26	1.23	1.23	0.77
CCl <sub>3</sub> H*	1.20	1.33	1.95	1.58
SiCl <sub>3</sub> H*	0.855	1.23	2.17	0.02
CH <sub>2</sub> Cl <sub>2</sub>	1.62	1.59	2.38	1.93
CF <sub>3</sub> Cl	0.50	0.57	0.21	0.46
CF <sub>2</sub> Cl <sub>2</sub>	0.55	0.57	0.29	0.34
CCl <sub>3</sub> F*	0.49	0.74	0.03	0.46
CH <sub>2</sub> FCI	1.82	1.79	2.20	1.91
CH <sub>3</sub> SiH <sub>3</sub>	0.73	0.76	0.65	1.81
CH <sub>3</sub> SiH <sub>2</sub> F	1.71	1.84	1.85	1.79
CH <sub>3</sub> SiHF <sub>2</sub>	2.11	2.56	2.56	2.53
CH <sub>3</sub> SiF <sub>3</sub>	2.33	1.98	1.86	
CH <sub>3</sub> SiCl <sub>3</sub> *	1.87	2.13	3.10	1.66
CH <sub>2</sub> CHCl	1.44		2.11	1.62
HCCCl	0.44	0.65	1.47	1.03
CiCN	2.80	1.89	1.07	1.64
COCl <sub>2</sub> *	1.19	0.49	0.42	0.37
CSCl <sub>2</sub> *	0.28	0.37	2.40	1.38

<sup>a</sup> Molecules used in the fitting process for  $\frac{1}{2}(I + A)_\mu$  are followed by an asterisk. <sup>b</sup> A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.

predicted CNDO barriers considerably (too much so in the case of Si<sub>2</sub>H<sub>6</sub>). While Ewig et al. also find such an increase for CH<sub>3</sub>SiH<sub>3</sub>, it is much smaller. Thus, while augmenting the INDO basis with d orbitals will probably improve the results, an effect the size of that shown in Table XIV is likely to be an artifact.

## V. Dipole Moments

The predicted dipole moments, calculated at the experimental geometries, are compared with the experimental values in Tables XV and XVI. The previously published<sup>2</sup> BH INDO and SPD' dipole moments are also included in these tables since the latter two methods were found to be the most reliable earlier. A considerable improvement is found for predicted dipole moments of molecules containing Si and Cl. With the exception of CiCN and COCl<sub>2</sub>, none of the predicted magnitudes is drastically out of line. The level of agreement for

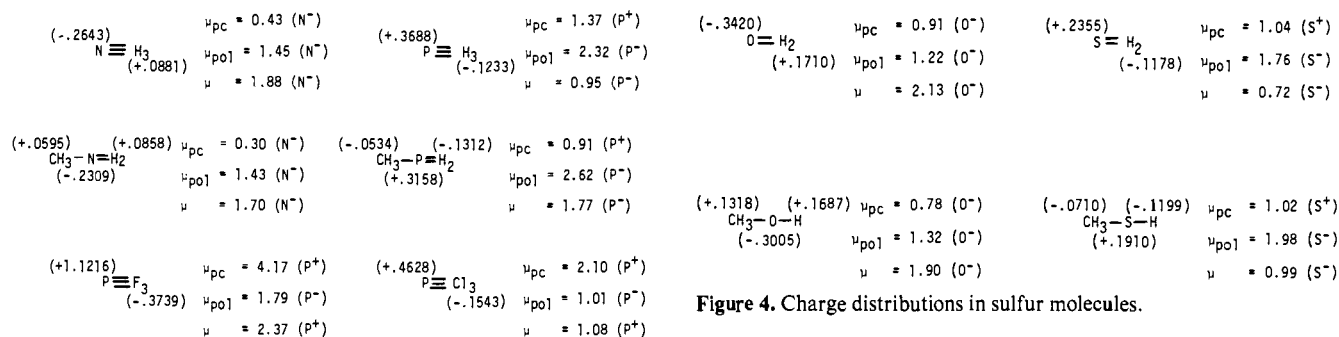


Figure 3. Charge distributions in phosphorus molecules.

Table XVI. Dipole Moments for Molecules Containing P or S (D)

Molecule <sup>a</sup>	Expt <sup>b</sup>	INDO	BH	SPD'
PH <sub>3</sub> *	0.578	0.95	2.62	0.61
PF <sub>3</sub> *	1.03	2.37	0.89	0.46
PCl <sub>3</sub> *	0.80	1.08	0.83	0.24
POF <sub>3</sub> *	1.69	1.81	1.97	2.44
POCl <sub>3</sub> *	2.37	1.89	0.54	2.29
PSF <sub>3</sub> *	0.633	0.90	4.24	1.43
PSCl <sub>3</sub> *	1.42	1.13	2.80	1.20
CH <sub>3</sub> PH <sub>2</sub> *	1.10	1.77	2.90	2.33
H <sub>2</sub> S*	0.937	0.72	2.72	1.32
CH <sub>3</sub> SH*	1.28	0.99	2.76	2.29
SO <sub>2</sub> *	1.61	2.79	1.71	1.58
SF <sub>4</sub>	1.0	2.07	1.03	0.33
COS	0.712	0.08	2.78	1.00
HNCS	1.72	2.18	4.81	3.05
CH <sub>3</sub> SCN	3.34	2.65	2.71	2.76
CH <sub>3</sub> NCS	3.59	2.08	5.18	3.55
SOF <sub>2</sub> *	1.618	3.34	2.40	2.03
SOCl <sub>2</sub> *	1.452	2.37	1.48	1.79
SiCl <sub>2</sub> *	1.04	1.32	0.13	

<sup>a</sup> Molecules used in the fitting process for  $\frac{1}{2}(I + A)_\mu$  are followed by an asterisk. <sup>b</sup> A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.

molecules containing P and, particularly, S (Table XVI) is considerably worse. Even so, there is substantial improvement relative to BH INDO and the results are only slightly worse than those for SPD'. Part of the difficulty with regard to phosphorus and sulfur compounds is that such molecules containing hydrogen or methyl groups want rather different values for the Mulliken electronegativity parameters from molecules containing more electronegative substituents (e.g., F, Cl, O). As a result, the final parameters, chosen using the function  $f_2$  as described above, are a compromise between the two types of molecules.

The reliability of INDO for predicting dipole moments is put in more quantitative terms with the error analysis presented in Table XVII. This table compares the average value of  $f_2$  (eq 3) for INDO, BH INDO, and SPD'. Also listed is  $\bar{f}_3$ ,

$$\bar{f}_3 = 1/N \sum_i |\mu_i^{\text{calcd}} - \mu_i^{\text{expt}}| / \mu_i^{\text{exp}} \quad (4)$$

which is more directly related to the average percent deviation from experiment. The improvement relative to BH INDO is dramatic, with  $\bar{f}_2$  smaller by an order of magnitude and  $\bar{f}_3$  smaller by a factor of 3. The improvement relative to SPD' is smaller, but still significant. As mentioned above, it is apparent that molecules containing sulfur are in worst agreement with experiment, the average percent deviation being more than 50%. In contrast, molecules containing Si and/or Cl deviate from the observed values by an acceptable average of 20%.

A further test of the agreement between theory and exper-

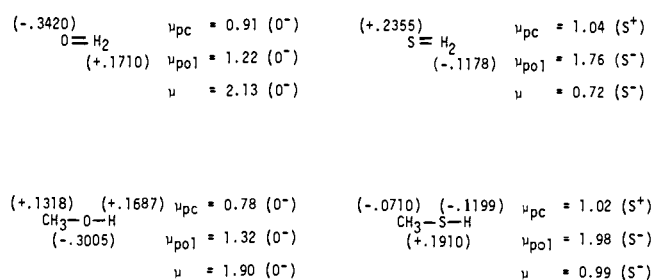


Figure 4. Charge distributions in sulfur molecules.

Table XVII. Error Analysis for Dipole Moments<sup>a</sup>

	INDO	BH	SPD'
$\bar{f}_2$ (Si, Cl)	0.079	3.310	1.088
$\bar{f}_2$ (P)	0.538	6.152	0.482
$\bar{f}_2$ (S)	0.406	1.623	0.215
$\bar{f}_2$	0.260	3.415	0.759
$\bar{f}_3$ (Si, Cl)	0.200	0.891	0.625
$\bar{f}_3$ (P)	0.475	1.619	0.540
$\bar{f}_3$ (S)	0.546	0.893	0.386
$\bar{f}_3$	0.354	1.038	0.544
<10%	10	8	9
<20%	15	14	13
<30%	24	15	15
<50%	30	20	24

<sup>a</sup> <N%> is the number of molecules with a calculated dipole moment which deviates from experiment by no more than N%.

iment is the number of molecules for which the calculated dipole moment is within a particular percent deviation of the observed value. As shown in Table XVII, the greatest improvement in the present method, according to this criterion, is in the 20–30% deviation range. More than half the molecules studied deviate from experiment by less than 30% and  $\frac{3}{4}$  of the molecules are within 50%.

For a semiempirical method, the ability to reproduce observed trends is at least as important as the prediction of absolute values for properties. It is here that previous methods have proved most disappointing<sup>2</sup> since many important trends in dipole moments are not predicted correctly. In most cases this situation is corrected with the present parametrization. Two striking examples are phosphine vs. ammonia (exptl  $\mu = 1.470^2$ ) and hydrogen sulfide vs. water (exptl  $\mu = 1.85 \text{ D}^2$ ). In both cases the second-row hydride is observed to have a much smaller dipole moment, and only the present method reproduces this trend. In order to dissect the dipole moments of first- and second-row hydrides, recall<sup>7</sup> that, within the INDO approximation, the dipole moment may be written as the sum of a point charge ( $\mu_{\text{pc}}$ ) and a polarization contribution ( $\mu_{\text{poi}}$ ):

$$\mu = \mu_{\text{pc}} + \mu_{\text{poi}} \quad (5)$$

The charge distributions and components of the dipole moments are depicted in Figures 3 (NH<sub>3</sub> and PH<sub>3</sub>) and 4 (H<sub>2</sub>O and H<sub>2</sub>S). In NH<sub>3</sub>, the dominant contribution is from  $\mu_{\text{poi}}$ , with both components having N at the negative end. In phosphine the point charge contribution is much larger. This is due in part to the greater charges and in part to geometry (longer bonds and smaller angles); however, in this case phosphorus is at the positive end. Thus, even though  $\mu_{\text{poi}}$  has the opposite sign and is larger than that in NH<sub>3</sub> (owing to the more diffuse lone pair on P), the dipole moment in PH<sub>3</sub> is much smaller than that in NH<sub>3</sub>. A similar argument obtains for H<sub>2</sub>O vs. H<sub>2</sub>S.

Related to the trends discussed above is the effect of methyl substitution on the four hydrides. In the first-row molecules methyl substitution leads to a decrease in dipole moment, and

**Table XVIII.** Dipole Moments for Molecules Containing Na and Al (D)

Molecule	Expt	INDO <sup>e</sup>	MB <sup>f</sup>
NaH	6.962 <sup>a</sup>	6.05 (6.71)	
NaF	8.19 <sup>b</sup>	6.64 (6.87)	5.07
NaCl	9.0 <sup>c</sup>	6.92 (7.32)	7.42
AlH	0.170 <sup>a</sup>	0.52	
AlF	1.53 <sup>d</sup>	0.33	0.33
AlCl	1-2 <sup>d</sup>	0.08	0.66

<sup>a</sup> Extended basis ab initio calculation by P. E. Cade and W. Huo, *J. Chem. Phys.*, **45**, 1063 (1966). <sup>b</sup> R. K. Bauer and H. Lew, *Can. J. Phys.*, **42**, 830 (1964). <sup>c</sup> A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1964. <sup>d</sup> D. R. Lide, *J. Chem. Phys.*, **42**, 1013 (1965). <sup>e</sup> The values in parentheses are obtained using  $\zeta_{\text{Na}} = 1.0$  and  $\beta_{\text{Na}}^c = -1.0$ . <sup>f</sup> Minimal basis ab initio results optimal exponents: ref 4.

this has been attributed to a bond alternation effect in the point charges. In contrast, as seen in Table XVI, methyl substitution in the second-row hydrides leads to an increase in dipole moment. This effect is reproduced only by the present method, and, as shown in Figures 3 and 4, the origin of the latter trend is more complicated than that for the first row. On going from NH<sub>3</sub> to CH<sub>3</sub>NH<sub>2</sub> the polarization component is virtually constant, so the change in dipole moment can reasonably be discussed in terms of point charges. Such is not the case for methylation of phosphine. Here, the polarization component increases by a nonnegligible amount. In addition,  $\mu_{\text{pc}}$  is reduced owing to charge alternation; however, since the point charge component has phosphorus at the positive end, the reduction in the magnitude of  $\mu_{\text{pc}}$  augments the increase in  $\mu_{\text{pol}}$  and results in a much larger dipole moment. For H<sub>2</sub>S vs. CH<sub>3</sub>SH, the change in  $\mu_{\text{pc}}$  is small, so the increase in the predicted dipole moment is smaller than the observed increase. Note also that INDO predicts methylphosphine to have a slightly larger dipole moment than methylamine, whereas the reverse is found to be the case experimentally.

The steady increase in dipole moment from PH<sub>3</sub> to PCl<sub>3</sub> is also reproduced by the new parametrization, whereas previous methods predicted too large a dipole moment for PH<sub>3</sub> (BH) or too small a value for PF<sub>3</sub> (SPD'). As shown in Figure 3, the point charge component for all three molecules has phosphorus at the positive end, while the sign is reversed for  $\mu_{\text{pol}}$ . As the magnitude of  $\mu_{\text{pc}}$  increases (from H to Cl to F) this component dominates the overall moment, and the sign is P<sup>+</sup>X<sup>-</sup> for PF<sub>3</sub> and PCl<sub>3</sub>. The charge shift is apparently too large in PF<sub>3</sub>, and this results in too large a theoretical dipole moment by a factor of 2.

With regard to other trends in Table XVI, the increase in dipole moment from PSF<sub>3</sub> to PSCl<sub>3</sub> to POF<sub>3</sub> to POCl<sub>3</sub> is now predicted correctly, although the value of POCl<sub>3</sub> is too small. This trend is not handled properly by any of the previous methods. While the magnitudes for SOF<sub>2</sub> and SOCl<sub>2</sub> are much too large, the order is correct; however, the observed order is reversed for CH<sub>3</sub>NCS vs. HNCS and for CH<sub>3</sub>NCS vs. CH<sub>3</sub>SCN.

As might be expected from the previous discussion of silicon and chlorine compounds, most of the experimental trends are correctly reproduced for the molecules in Table XV. An example of this is the decrease in dipole moment which appears to be typical when Si is substituted for C in such systems. The smaller dipole moment of SiH<sub>3</sub>F relative to CH<sub>3</sub>F (exptl  $\mu = 1.85$  D) appears to be due primarily to the polarization component. This is shown in Figure 5, where it is seen that  $\mu_{\text{pol}}$  reinforces  $\mu_{\text{pc}}$  for the carbon compound, but is slightly positive for SiH<sub>3</sub>F. A similar result is found for SiH<sub>3</sub>Cl relative to CH<sub>3</sub>Cl; however, in this case the decrease in  $\mu$  is too small.

$(-.0309)$ $\text{H}_3\text{C}\equiv\text{C}-\text{F}$ $(+.3236)$	$(-.2310)$ $\mu_{\text{pc}} = 1.35$ (F <sup>-</sup> ) $\mu_{\text{pol}} = 0.34$ (F <sup>+</sup> ) $\mu = 1.69$ (F <sup>-</sup> )	$(-.0167)$ $\text{H}_3\text{C}\equiv\text{C}-\text{Cl}$ $(+.1090)$	$(-.0588)$ $\mu_{\text{pc}} = 0.42$ (Cl <sup>-</sup> ) $\mu_{\text{pol}} = 0.99$ (Cl <sup>-</sup> ) $\mu = 1.41$ (Cl <sup>-</sup> )
$(-.2635)$ $\text{H}_3\text{Si}\equiv\text{Si}-\text{F}$ $(+.1966)$	$(-.4061)$ $\mu_{\text{pc}} = 1.25$ (F <sup>-</sup> ) $\mu_{\text{pol}} = 0.04$ (F <sup>+</sup> ) $\mu = 1.21$ (F <sup>-</sup> )	$(-.2118)$ $\text{H}_3\text{Si}\equiv\text{Si}-\text{Cl}$ $(+.8386)$	$(-.2032)$ $\mu_{\text{pc}} = 0.54$ (Cl <sup>-</sup> ) $\mu_{\text{pol}} = 0.78$ (Cl <sup>-</sup> ) $\mu = 1.32$ (Cl <sup>-</sup> )

**Figure 5.** Charge distributions in Si and Cl molecules.

Similarly, the trend for SiCl<sub>3</sub>H vs. CCl<sub>3</sub>H is correct but too small. For both of the latter two pairs of molecules BH INDO has the trend reversed relative to the experimental one, while SPD' has the ordering correct, but the magnitudes for the carbon compounds are rather poor. The dipole moments for CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, and CCl<sub>3</sub> are all properly predicted to be small and to be similar in magnitude; however, CH<sub>3</sub>Cl is incorrectly predicted to have a smaller moment than CH<sub>2</sub>Cl<sub>2</sub>.

Finally, although the experimental data are scarce, it is of interest to briefly consider dipole moments for molecules containing Na and Al. These are listed in Table XVIII. The Na-containing molecules are correctly predicted to have rather large dipole moments and the steady increase observed from NaH to NaCl is reproduced, although the increase is too small. It is interesting to note as well that the agreement with experiment is improved when the revised parameters are used for Na. The predicted moment for AlH is too large, while those for AlF and AlCl appear to be much too small. Note, however, that the level of agreement between INDO and experiment in Table XVIII is generally similar to that found earlier<sup>4</sup> using a minimal basis set of Slater orbitals with optimized valence exponents.

## VI. Conclusions

Overall, the general level of agreement between theory and experiment has been greatly improved by a careful reparametrization of the semiempirical method. The reliability of the method now appears to be comparable to that for the first row. Particularly with regard to geometries, an INDO calculation should be a viable alternative to a time-consuming minimal basis ab initio calculation. While bond lengths connecting second-row atoms with electronegative atoms in the first row are typically overestimated, the errors are much improved relative to earlier methods. Based on previous experience,<sup>3,4</sup> the errors in such bond lengths should be improved by adding d orbitals to the basis set. While d orbitals will clearly be important for predicting structures of hypervalent molecules,<sup>9</sup> it is encouraging that the minimal basis method presented here represents an improvement over previous semiempirical methods which included d orbitals.<sup>10,16</sup>

Predicted dipole moments for molecules containing Si and Cl are in good agreement with experimentally observed magnitudes and trends. While the reliability is worse for phosphorus and particularly S, similar problems were encountered for oxygen-containing molecules.<sup>7</sup> Thus, this may represent a basic failing inherent in the INDO method.

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## On the Interpretation of $^{13}\text{C}$ Spin-Lattice Relaxation Resulting from Ring Puckering in Proline

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**Abstract:** A calculation of  $^{13}\text{C}$  relaxation parameters for a system undergoing overall isotropic motion as well as internal conformational fluctuation between two stable states is presented. Dependence of  $T_1$  on the lifetimes of the two conformations, the angle defined by the particular C-H vector and the effective axis about which it rotates, and the range through which it rotates are considered. Relaxation data for proline and proline-containing peptides have been analyzed on the basis of several models for proline puckering: interconversion between two envelope forms with  $\text{C}\gamma$  puckered, interconversion between two  $\text{C}^\beta$ - $\text{C}\gamma$  half-chair forms, and an intermediate case. Consideration of the  $^{13}\text{C}$   $T_1$  values for each proline carbon indicates that for most cases the two stable conformational states correspond to approximate  $\text{C}^\beta$ - $\text{C}\gamma$  half-chairs with  $\text{C}\gamma$  exhibiting a somewhat greater angular displacement than  $\text{C}^\beta$ . Reasonable values for the  $NT_1^\gamma/NT_1^\alpha$  ratio can be obtained by requiring roughly equal lifetimes  $\sim 10^{-11}$ - $10^{-12}$  s for the two states and a typical range of motion for the  $\text{C}\gamma$ -H vectors  $\sim 50$ - $70^\circ$ . These results appear to be consistent with available theoretical calculations, x-ray data, and conclusions based on  $^1\text{H}$ - $^1\text{H}$  scalar coupling studies.

### Introduction

$^{13}\text{C}$  NMR offers a uniquely powerful tool for studying molecular dynamics due to the dominance of the spin relaxation by the dipolar interaction with the directly bonded protons.<sup>1</sup> The measured relaxation times can, with the aid of an appropriate model, be directly used to obtain information about the motion of individual C-H bonds. This situation differs from that encountered for most other nuclei; in particular, in  $^1\text{H}$  NMR studies it is necessary to separate intra- and intermolecular contributions as well as to sort out all of the intramolecular interactions which may be significant.

The relaxation behavior of proline, both as the free amino acid and incorporated into various peptides, has stimulated considerable interest due to the marked differences in the  $T_1$  values for the carbons in the pyrrolidine ring.<sup>2-20</sup> Such differences can be interpreted to reflect anisotropic motion of a basically rigid structure, internal motion such as would arise from a rapid interconversion of puckered conformations, or a combination of effects. The generality of these differences in relaxation time makes an explanation based primarily on anisotropic motion unlikely since the anisotropy exhibited by different peptides is likely to be very different. A recent quantitative evaluation of the relaxation effects of motional anisotropy based on crystallographic data substantiates this conclusion.<sup>21</sup> Of course, differences in motional anisotropy of the peptide backbone may contribute to the differences observed in various peptides. Attempts to describe the relaxation behavior in terms of internal motion have been limited to use of a free internal rotation model<sup>13</sup> and to an approximation in which the different relaxation times reflect a different effective

correlation time for each carbon in the ring.<sup>5,6</sup> The interpretation of internal diffusion coefficients or correlation times deduced from the application of such models is, however, ambiguous. For example, if the ring alternates between only two conformational states, the lifetime of each conformation will be the same for all carbons in the ring, but  $T_1$  differences can still be predicted due to differences in the angular factors involved, as is shown in the present calculation.

The approach considered here is based on a bistable system able to alternate between two different conformations. Such an approach leads to an evaluation of the observed relaxation times in terms of the overall diffusion rate, the lifetimes of the two states, the angle between the particular C-H vector, and the effective axis about which it rotates due to the jump, and the range through which the C-H vector jumps. This calculation probably represents an oversimplification for the proline ring system which may be able to adopt many puckered conformations. It can be justified on several grounds: (1) Studies of  $^1\text{H}$ - $^1\text{H}$  coupling constants indicate the existence of a conformational equilibrium between two equally populated conformations.<sup>22-25</sup> Roughly equivalent stabilities are also required based on the present relaxation calculations using the two-state model. (2) Theoretical energy calculations indicate the existence of two energy minima corresponding roughly to the states considered in the present calculations.<sup>26-28</sup> (3) The range through which the various C-H vectors must move to produce the observed relaxation rates is consistent with the degree of puckering observed in crystallographic studies.<sup>28,29</sup> (4) Development of the present model makes possible an evaluation of the relaxation effect of several models for internal