Ab initio computation of force constants. I. The second and third period hydrides*

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The force method has been employed to calculate the force constants of HF, H_2O, NH_3, CH_4, HCl, H_2S, PH_3, and SiH_4. The computations were performed using wavefunctions generated by both the STO-3G and 4-31G basis sets that are standard in the Gaussian 70 program system. The 4-31G basis set provides reliable harmonic force constants, but those computed with the STO-3G basis set are poor. Cubic force constants computed at the 4-31G level are fair to very good. Cubic stretching force constants are reproduced especially well, regardless of the basis set. Quartic stretching force constants are good, but quartic bending constants are in error. A component analysis has been developed and relations have been found that may be useful for qualitative and quantitative discussions.

I. INTRODUCTION

The computation of force constants *ab initio* has become both practical and reliable in recent years. The force method, applied by Pulay,[1] has been used successfully to calculate the harmonic force fields of a variety of small molecules.[2-7] For moderate size basis sets, such calculations yield force constants that are within 20% of the experimental harmonic force constants.[3] In the case of ethylene, the theoretical calculations of Pulay and Meyer[6] were able to distinguish between two alternative experimental force fields. The effect of basis set size has been investigated in detail for methane.[3] Meyer and Pulay have shown that so long as the basis set is not severely contracted, a medium size basis set performs approximately as well as a near Hartree–Fock quality basis set.

The computations reported by Pulay have been performed using various Gaussian lobe basis sets. The purpose of the present paper is to describe the results of calculations using two Cartesian Gaussian basis sets, STO-3G and 4-31G,[8] which are standard in the Gaussian 70 program system.[9] With the increasing use of such basis sets, it is important to establish their utility in the computation of vibrational force fields. Once this has been achieved, forces and force constants obtained from readily available wavefunctions using these standard basis sets can be employed to study a rich variety of problems in chemistry and spectroscopy.

II. METHOD

The theory required for the computation of force constants by the force method has been published by Pulay.[1] The force constants are the second derivatives of the energy with respect to the coordinates of the atoms in the molecule. In the force method the forces, i.e., the negative of the first derivative of the total energy with respect to the positions of the atoms, are computed analytically. These are then differentiated numerically to obtain the force constants. The general theory of energy derivatives within the SCF framework has been outlined by several authors.[1,10] The total SCF energy is expressed as

$$E = 2 \sum_{m,n} D_{m,n} h_{m,n} + \sum_{m,n,o,p} P_{m,n,o,p}(mn \,|\, op) + V_{NN} , \qquad (2.1)$$

where $D_{m,n} = \sum_i^{occ} C_{i,m} C_{i,n}$ is an element of the one electron density matrix, $C_{i,m}$ is an element of the ith orbital vector,

$$P_{m,n,o,p} = [2 D_{m,n} D_{o,p} - \tfrac{1}{2}(D_{m,o} D_{n,p} + D_{m,p} D_{n,o})] ,$$

$h_{m,n}$ is a one electron integral and $(mn \,|\, op)$ is a two electron integral. The first derivative of the total energy with respect to a variable A is given by:

$$\frac{\partial E}{\partial A} = 2 \sum_{m,n} D_{m,n} \frac{\partial h_{m,n}}{\partial A} + \sum_{m,n,o,p} P_{m,n,o,p} \frac{\partial (mn \,|\, op)}{\partial A}$$

$$- 2 \sum_{m,n} D'_{m,n} \frac{\partial S_{m,n}}{\partial A} + \frac{\partial V_{NN}}{\partial A} \qquad (2.2)$$

where $D'_{m,n} = \sum_i^{occ} \epsilon_i C_{i,m} C_{i,n}$, ϵ_i is the ith orbital energy, and $S_{m,n}$ is an overlap integral. These formulas require only the unperturbed SCF wavefunction. Consequently the computation of the forces requires only the additional integral derivatives of Eq. (2.2). The equations for the second derivatives are also given in the literature,[10] but are somewhat cumbersome to handle. For these, the full first order perturbed density matrix is needed and must be calculated in a self-consistent manner. At the present, it appears that it is more efficient to calculate the second derivative numerically from the first derivative computed at several points. The third derivatives can be obtained numerically in the same way.

To aid in the analysis of the force field, the forces and force constants can be broken down into various components. A convenient and useful partitioning scheme is given in Eq. (2.3):

$$\frac{\partial E}{\partial A} = 2 \sum_{m,n} \langle m | \frac{\partial \hat{V}_{NE}}{\partial A} | n \rangle D_{m,n} + 2 \sum_{m,n} \left(\langle \frac{\partial m}{\partial A} | \hat{V}_{NE} | n \rangle + \langle m | V_{NE} | \frac{\partial n}{\partial A} \rangle \right) D_{m,n}$$

$$+ 2 \sum_{m,n} \frac{\partial}{\partial A} \langle m | \hat{T} | n \rangle D_{m,n} + \sum_{m,n,o,p} \frac{\partial(mn|op)}{\partial A} P_{m,n,o,p} - 2 \sum_{m,n} \frac{\partial S_{m,n}}{\partial A} D'_{m,n} + \frac{\partial V_{NN}}{\partial A} . \tag{2.3}$$

The first term of Eq. (2.3) arises from the derivative of the Hamiltonian with respect to the coordinates of the nuclei, which reduces to the derivative of the nuclear-electron attraction operator [V_{NE}(operator)]. The second to fifth terms arise from the derivatives of the energy with respect to the positions of the basis functions. In the LCAO approach, the basis functions are centered on the nuclei and move with them. Such contributions can be decomposed into nuclear-electron attraction [V_{NE}(wfn)], kinetic, and two electron terms. The fifth term arises from the change in the orbital coefficients when the basis functions are moved. The last term is the change in the nuclear–nuclear repulsion energy.

III. CALCULATIONS

The SCF computations were performed with the Gaussian 70 program system[9] using the standard STO-3G and 4-31G basis sets.[8] A standard extended basis set for silicon did not exist and was therefore constructed from the standard STO-4G basis set for silicon. The inner shells were left unchanged, while the contraction scheme for the valence shell was altered to conform to the 4-31G basis sets for third period elements. The scaling factors ζ for the valence shells were optimized for silane ($\zeta_{inner} = \zeta_{outer} = 1.952$, constrained to be equal).

A series of programs has been written to compute the forces and their components from wavefunctions that use s and p type Cartesian Gaussians.[11] Both this program system and Gaussian 70 exploit the fact that the STO-3G and 4-31G basis sets have common Gaussian exponents shared between contracted s and p functions.[8] This allows considerable factoring and simplification during the evaluation of the integrals. The net result is an order of magnitude reduction in the computational time for both the integrals[9] and their derivatives.[11] The calculation of the forces requires approximately the same amount of computer time as the complete SCF calculation.

The transformations to internal coordinates for the forces are performed as outlined in Ref. 1. Force constants can be calculated at either the theoretical equilibrium geometry or the experimental geometry.[12] At the geometry of interest and at small displacements from this geometry the energy and the forces are calculated. Displacements of ± 0.05 Å for bond lengths and ± 2.5° for angles are employed. These data are then used to calculate the harmonic and cubic force constants and their components.

The diagonal harmonic force constants can be refined and a rough estimate of the principal quartic force constants obtained by fitting the energies and forces to a quartic equation, i.e.,

$$E = \tfrac{1}{2}K_2 q^2 + \tfrac{1}{6}K_3 q^3 + \tfrac{1}{24}K_4 q^4 ,$$

$$F = K_2 q + \tfrac{1}{2}K_3 q^2 + \tfrac{1}{6}K_4 q^3 , \tag{3.1}$$

where q is the displacement of the internal coordinate from its equilibrium value.

Calculations were performed on a CDC 6600 computer at the Universita di Bologna and the IBM 360/50 and Burroughs B6700 computers of Queen's University at Kingston.

IV. RESULTS AND DISCUSSION

A. The second period hydrides

The computed force constants of HF, H_2O, NH_3, and CH_4 are collected in Tables I–IV. These show, in addition to the present work with the STO-3G and 4-31G basis sets, the force constants computed by Pulay with a standard 73/3 +1 basis set and with more elaborate basis sets. A comparison with calculations of force constants using techniques other than the force method is not made here since this has already been done by Pulay.

The calculations of the quadratic, cubic, and quartic force constants of hydrogen fluoride are summarized in Table I. The values for the 73/3 + 1 basis set were calculated directly from Table II of Ref. 5 with the aid of Eq. (3.1). The agreement between f_{rr} of the 4-31G calculation and experiment is very good. Not surprisingly f_{rr} is reproduced poorly with the minimal basis set (STO-3G). The agreement among the cubic force constants is, however, unexpectedly good. Despite a 45% error in the harmonic force constant computed with the STO-3G basis set, the cubic force constant is in error by only 15%. The calculated quartic force constants are also quite satisfactory.

Gathered in Table II are the force constants of water. The minimal basis set calculation is rather poor in reproducing bending and interaction force constants. The

TABLE I. Force constants of hydrogen fluoride.[a]

Force constant	Basis set			
	73/3 + 1[b]	STO-3G[c,d]	4-31G[c,d]	Experimental[e]
f_{rr}	10.751	14.126	9.874	9.658
f_{rrr}	− 75.06	− 82.07	− 70.11	− 71.1
f_{rrrr}	504.89	432.54	584.70	478.

[a]Units: quadratic stretching force constants, mdyne/Å; cubic stretching force constants, mdyne/Å^2; quartic stretching force constants, mdyne/Å^3.
[b]Calculated from data in Ref. 5.
[c]Present work using the experimental bond length $r_e = 0.917$ Å.
[d]Two electron integrals contributing less than 10^{-6} a.u. to the total energy were not used in calculating the forces.
[e]Reference 13.

TABLE II. Force constants of water.[a]

Force constant	Basis set				
	$73/3+1^b$	$95/41+2^b$	STO-3G^{c,d}	4-31G^{c,d}	Experimental^e
f_{rr}	9.372	9.158	10.185	8.707	8.454
$f_{rr'}$	−0.156	−0.172	−0.475	−0.128	−0.101
$f_{\theta\theta}$	0.751	0.780	1.307	0.793	0.697
$f_{r\theta}$	0.292	0.288	0.311	0.325	0.219
f_{rrr}	−62.744	−60.800	−57.135	−61.397	−59.366 ± 3.01
$f_{rrr'}$	0.281	0.219	0.756	−0.141	0.253 ± 1.5
$f_{rr\theta}$	−0.278	−0.481	−0.591	−0.002	0.404 ± 0.2
$f_{\theta\theta r}$	−0.163	−0.409	−0.500	−0.426	−0.225 ± 0.1
$f_{\theta\theta\theta}$	−0.745	−0.855	−1.063	−0.912	−0.877 ± 0.1
f_{rrrr}	385.17	437.58	290.20	413.18	384.08 ± 62.5
$f_{\theta\theta\theta\theta}$	−0.80	25.16	−37.95	−30.71	−0.07 ± 0.2

[a]Units: quadratic, cubic, and quartic bending force constants, mdyne-Å; stretch–bend and stretch–bend–bend force constants, mdyne; stretch~stretch–bend force constants, mdyne/Å; for other units see Table I.
[b]Reference 2.
[c]Present work. Geometry: STO-3G, $r=0.990$, $\theta=100.0$; 4-31G, $r=0.957$, $\theta=110.6$, taken from previous optimizations.
[d]Footnote (d) Table I.
[e]Reference 14.

4-31G calculation appears to produce harmonic force constants as well as or better than the larger 95/41 +2 basis set.[2] The diagonal cubic constants are predicted satisfactorily by all four basis sets as is the quartic stretching force constant. The quartic bending term, however, is unsatisfactory.

The ammonia force fields are presented in Table III. The STO-3G and one of the 4-31G computations were performed at the optimized geometry of the 4-31G calculation. This differs substantially from the experi-mental geometry ($\theta=113°$, $r=0.995$ Å calculated vs $\theta=107°$, $r=1.012$ Å observed), and accounts for the poor agreement in the harmonic force constants. The error in the optimum geometry reflects a deficiency in the nitrogen 4-31G basis set, and this deficiency will in turn affect the quality of the computed force constants. The inadequacy of the nitrogen basis set has been noted previously.[8b] However, when the experimental geometry is used for the 4-31G calculation, the improvement is quite striking, resulting in force constants that are ap-proximately of the same quality as those produced by the 73/3 +1 basis set. This constitutes an excellent exam-ple of the argument given by Schwendeman.[12]

The methane force fields are collected in Table IV. Because of the problem of redundant valence coordi-nates, symmetry coordinates have been used. As in Tables I–III, the STO-3G calculation displays its char-acteristic overestimation of the stretching force con-stants. This is a feature of any basis set that is con-tracted to a minimal representation of the valence orbit-als. For example,[3] when the 95/4 basis set is con-tracted to a minimal basis, denoted as 95/4* in Table IV, the force constants are overestimated in a manner similar to the STO-3G calculations. A moderate amount of contraction is permissible. The 4-31G basis set is contracted to two shells in the valence region and per-forms approximately as well as the 73/3 +1 and the 95/4 basis sets, which are uncontracted in the valence region. The anharmonic constants agree well with each other. A previous estimate of the cubic stretching constant[16] is supported by the present calculations.

In summary, we find that while the STO-3G basis set does not provide spectroscopically useful harmonic

TABLE III. Force constants of ammonia.[a]

Force constant	$73/3+1^b$	$1061/51+1^b$	Basis set STO-3G^{c,d}	4-31G^{c,d}	4-31G^{d,e}	Experimental^f
f_{rr}	7.673	7.380	10.791	8.115	7.505	7.052
$f_{rr'}$	−0.063	−0.002	−0.264	−0.044	−0.020	0.015
$f_{\theta\theta}$	0.739	0.693	0.808	0.467	0.748	0.636
$f_{\theta\theta'}$	−0.067	−0.052	−0.067	−0.062	−0.071	−0.045
$f_{r\theta}$	0.064	0.034	0.208	0.066	0.045	0.146
$f_{r\theta'}$	0.271	0.219	0.357	0.288	0.301	0.322
f_{rrr}	−49.55	−44.95	−58.45	−53.46	−49.17	−46.12
$f_{rrr'}$	0.18		0.13	0.13	0.02	
$f_{rr\theta}$	−0.05		−0.37	0.02	−0.01	
$f_{rr\theta'}$	−0.05		−0.42	0.28	0.19	
$f_{\theta\theta\theta}$	−1.08	−0.85	−1.49	−0.93	−0.85	
$f_{\theta\theta\theta'}$	0.01		−0.09	−0.01	−0.01	
$f_{\theta\theta r}$			0.07	−0.10	−0.04	
$f_{\theta\theta r'}$	−0.12		−0.07	−0.15	−0.35	
f_{rrrr}	276.11		201.38	558.67	303.08	265.70
$f_{\theta\theta\theta\theta}$	−0.51		−139.29	509.61	15.24	

[a]Units: See Tables I and II.
[b]References 4 and 5.
[c]Present work. Geometry: $r=0.995$, $\theta=113.7$, previously optimized with the 4-31G basis set.
[d]Footnote (d) Table I.
[e]Present work. Geometry: $r=1.008$, $\theta=107.3$, experimental.
[f]Reference 14.

TABLE IV. Force constants of methane.[a]

Force constant	Basis set				STO–3G[d]	4–31G[d]	Experimental[e]
	73/3+1[b]	95/4[b]	95/4*[b,c]	953/41+1[b]			
F_{11}	5.770	5.567	7.146	5.578	7.038	5.617	5.842
F_{22}	0.708	0.656	0.756	0.642	0.836	0.674	0.581
F_{33}	5.626	5.387	7.264	5.382	7.339	5.445	5.382
F_{34}	0.235	0.248	0.165	0.221	0.091	0.131	0.225
F_{44}	0.668	0.646	0.743	0.612	0.814	0.667	0.579
f_{rr}	5.643				7.264	5.488	5.535
$f_{rr'}$	0.036				−0.075	0.043	0.153
f_{rrr}	−32.91				−35.24	−32.14	(−33.21)[f]
$f_{rrr'}$	0.14				0.16	0.12	
f_{rrrr}	161.03				171.99	171.31	

[a]Units: See Tables I and II.
[b]Reference 3,* denotes contractions to a minimal basis set.
[c]Contracted to a minimal basis representation.
[d]Present work using the experimental bond length $r_e = 1.093$ Å.
[e]Reference 15.
[f]Reference 16.

force constants, it can provide reasonable estimates of diagonal cubic and quartic stretching force constants. Diagonal cubic bending force constants are somewhat less reliable, but may still be useful. The 4-31G basis set, on the other hand, can provide good harmonic and diagonal cubic force constants. The stretching terms are more accurate than the bending terms. Calculated diagonal quartic stretching force constants are in good agreement with experiment. The standard nitrogen basis set should be used with caution and calculations performed at the experimental rather than the theoretical equilibrium geometry.

In Eq. (2.3) a partitioning scheme for the forces was defined. If the forces are differentiated numerically component by component it can be seen that the harmonic and cubic force constants can be decomposed in a similar manner. Table V contains some of the force constants and their components. There are two reasons for such a components analysis. Of all the components, only the V_{EE} term causes any difficulty in the calculation. Since it involves the two electron integrals, the computation of this term is as costly as the computation of the total energy. Thus if its computation could be circumvented, the calculation of force constants would be simplified

TABLE V. Components of force constants for second period hydrides.[a]

Force constant	V_{NE}(opr)	V_{NE}(wfn)	Kinetic	Components[b]		Nuclear	Total	Hellmann–Feynman
				V_{EE}	Coefficient			
HF								
f_{rr}	−32.70967	−63.21569	−13.40072	31.97739	6.48875	54.17577	10.11728	11.46610
f_{rrr}	98.75747	128.29351	−47.19619	−58.94023	−13.96012	−177.06220	−70.10776	78.30473
H$_2$O								
f_{rr}	−28.88895	−47.49069	12.06387	25.76103	4.45256	42.98118	8.87900	14.09223
$f_{rr'}$	−3.51588	−3.11594	0.34714	4.92109	0.24193	0.99417	−0.12748	−2.52171
$f_{\theta\theta}$	0.17053	7.58245	−0.80713	−6.20760	−0.67457	0.71921	0.78289	0.88974
f_{rrr}	73.19408	49.30229	−29.75200	−17.19208	−3.86234	−133.08715	−61.39720	−59.89307
NH$_3$								
f_{rr}	−24.37335	−29.87601	9.52002	17.17616	2.47442	32.71022	7.63147	8.33687
$f_{rr'}$	−1.00941	−2.34135	0.03425	2.44797	0.04071	0.88928	−0.01966	−0.12013
$f_{\theta\theta}$	−0.10114	8.14275	−0.82275	−6.51117	−0.69533	0.74074	0.75309	0.63960
$f_{\theta\theta'}$	−0.12754	−1.34407	0.14352	1.17506	0.08163	0.0	−0.07140	−0.12754
f_{rrr}	46.73366	10.28161	−15.85868	3.33505	0.96731	−94.63023	−49.17128	−47.89657
CH$_4$								
f_{rr}	−16.50419	−14.74606	6.13015	7.22678	0.94505	22.50744	5.55917	6.00325
$f_{rr'}$	−0.71033	−0.29335	−0.00684	0.66047	−0.17375	0.67675	0.04296	−0.03358
f_{rrr}	26.70521	−11.80060	−6.15797	15.29618	2.76608	−58.95198	−32.14309	−32.24678

[a]Units: See Tables I and II. [b]As defined by Eq. (2.3), and calculated with the 4-31G basis set.

TABLE VI. Force constants of hydrogen chloride.[a]

Force constant	Basis set		Experimental[d]
	STO-3G[b,c]	4-31G[b,c]	
f_{rr}	7.870	5.813	5.162
f_{rrr}	−36.82	−29.37	−28.7
f_{rrrr}	187.16	255.13	140

[a]Units: See Table I.
[b]Present work using the experimental geometry: $r_e = 1.2744$.
[c]Footnote (d) of Table I.
[d]Reference 13.

greatly. Secondly, a component analysis might lead to a better understanding of the behavior of force constants, in the same way that it has been helpful in the interpretation of barriers to rotation and inversion.[17]

For exact Hartree–Fock wavefunctions, one can invoke the Hellmann–Feynman theorem and proceed to calculate the forces from the V_{NE} (operator) term and the V_{NN} term. However, it is well established that most LCAO–SCF wavefunctions produce unacceptable Hellmann–Feynman forces (see Ref. 2 for examples). But if the error in the Hellman–Feynman forces is a constant or a slowly varying term, its derivative would be small and the force constant calculated from the Hellmann–Feynman forces could be close to the correct theoretical value. Reasonable, although not reliable, values are obtained for the diagonal harmonic force constants, while off-diagonal elements are incorrect by an order of magnitude. Consequently, Hellmann–Feynman force constants could be useful as a basis for a qualitative discussion of variations in force constants.

The Hellmann–Feynman diagonal cubic stretching force constants are in excellent agreement with the full calculation. This suggests that a very good approximation to the second derivative of the radial electronic distribution is possible. Therefore, even a smaller basis

TABLE VII. Force constants of hydrogen sulphide.[a]

Force constant	Basis set		Experimental[d]
	STO-3G[b,c]	4-31G[b,c]	
f_{rr}	5.467	3.903	4.284
$f_{rr'}$	−0.089	−0.017	−0.012
$f_{\theta\theta}$	1.186	0.853	0.754
$f_{r\theta}$	0.021	0.134	0.134
f_{rrr}	−24.24	−20.82	−23.34
$f_{rrr'}$	0.17	−0.03	0.22
$f_{rr\theta}$	−0.03	−0.07	−0.80
$f_{\theta\theta r}$	−0.31	−0.34	−0.10
$f_{\theta\theta\theta}$	0.78	−0.54	−0.126
f_{rrrr}	345.07	132.50	115.2
$f_{\theta\theta\theta\theta}$	161.62	267.62	0.0

[a]Units: See Tables I and II.
[b]Present work. Geometry: $r = 1.355$, $\theta = 95.77°$; previously optimized with the 4-31G basis set.
[c]Footnote (d) Table I.
[d]Reference 13.

TABLE VIII. Force constants of phosphine.[a]

Force constant	Basis set		Experimental[d]
	STO-3G[b,c]	4-31G[b,c]	
f_{rr}	4.208	2.994	3.445
$f_{rr'}$	−0.049	−0.003	−0.021
$f_{\theta\theta}$	1.206	0.861	0.733
$f_{\theta\theta'}$	−0.006	−0.037	−0.024
$f_{r\theta}$	0.039	0.024	−0.132
$f_{r\theta'}$	0.044	0.118	−0.076
f_{rrr}	−17.29	−13.89	
$f_{rrr'}$	0.08	−0.07	
$f_{rr\theta}$	−0.07	0.01	
$f_{rr\theta'}$	−0.10	−0.19	
$f_{\theta\theta\theta}$	−1.04	−0.73	
$f_{\theta\theta r}$	0.02	0.05	
$f_{\theta\theta r'}$	−0.42	−0.34	
f_{rrrr}	486.09	196.70	
$f_{\theta\theta\theta\theta}$	−80.56	58.00	

[a]Units: See Tables I and II.
[b]Present work. Geometry: $r = 1.433$, $\theta = 95.02$; previously optimized with the 4-31G basis set.
[c]Footnote (d) Table I.
[d]Reference 15.

set should be able to calculate acceptable cubic stretching force constants. This rationalizes the accuracy of the cubic stretching terms from the STO-3G calculation. However, such agreement is not found for other cubic force constants such as bending. The proper description of the flexibility in the angular distribution of the electrons is thus relatively difficult to obtain. This may account for the lower accuracy in the bending force constants.

For motions which have little anharmonicity, such as bending, one finds a "quasivirial" relationship between the total harmonic force constant and the kinetic term (i.e., the total is equal to the negative of the kinetic term). Thus for H–X–H bending motions only the kinetic term need be calculated to obtain an approximate value for the force constants, and such an approach might have qualitative utility. However, a similar relation for cubic force constants is not found.

B. The third period hydrides

The computed and experimental force constants of HCl, H_2S, PH_3, and SiH_4 are collected in Tables VI–IX. Unfortunately, no other calculations of these force constants by the force method are available for comparison at this time.

The minimal basis set reproduces harmonic force constants of the third period hydrides just as poorly as those of the second period hydrides. In HCl, for example (Table VI), f_{rr} is overestimated by $\simeq 50\%$. However, the error in the cubic and quartic force constants is less than 35%. The extended basis set calculations for f_{rr} and f_{rrr} are in excellent agreement with experiment, but the value of f_{rrrr} is rather poor.

The hydrogen sulphide computations, Table VII, parallel those of water. The harmonic bending and

TABLE IX. Force constants of silane.[a]

Force constant	Basis set		Experimental[c]
	STO-3G[b]	4-31G[b]	
F_{11}	3.879	3.020	2.840
F_{22}	0.621	0.479	0.404
F_{33}	3.907	2.867	2.742
F_{34}	0.029	0.064	0.034
F_{44}	0.739	0.567	0.496
f_{rr}	3.900	2.906	
$f_{rr'}$	-0.007	0.038	
f_{rrr}	-14.75	-12.50	
$f_{rrr'}$	-0.04	-0.04	
f_{rrrr}	51.89	55.33	

[a]Units: See Tables I and II.
[b]Present work using the experimental geometry, $r_e = 1.48$Å.
[c]Reference 15.

interaction constants are poor with the minimal basis set but quite good with the extended basis set. Surprisingly, a value of f_{rr} lower than the experimental is calculated with the extended basis set. The cubic stretching constant is represented well at both levels of calculation, whereas other cubic force constants are poor. The extended basis set, but not the minimal basis, is satisfactory for the quartic stretching force constants. As with the second period hydrides, quartic bending constants are very poor.

For phosphine, Table VIII, the minimal basis set force constants are characteristic. The bending and interaction force constants are poor and the harmonic stretching constant is too high. The extended basis set provides results closer to the experimental harmonic force

field. As in hydrogen sulphide, f_{rr} is underestimated. Based on the small change in some of the cubic force constants on going from a minimal to an extended basis set, the diagonal cubic stretching and bending constants are expected to be fair to good. The quartic bending term is most likely unrealistic. The reliability of the quartic stretching constant for this molecule is uncertain.

Table IX contains the results of the computations on silane. The redundancy of the angle coordinates is again removed by expressing the force field in terms of symmetry coordinates. The usual overestimation of the diagonal harmonic force constants is observed when the computation is carried out at the minimal level. Much better agreement is found with the extended basis set calculation. The fact that the agreement is good with this crudely extended silicon basis set is justification for its continued use. As in methane, anharmonic force constants calculated at both levels agree well with each other.

The conclusions for the basis sets of third period elements parallel those of the second row elements. From a spectroscopic point of view, only the extended basis sets are reliable for the prediction of harmonic force constants. Diagonal cubic and quartic stretching constants are also useful when computed at the extended basis set level.

The component analyses of the force constants, Table X, reveal the same features found for the second row hydrides in Table V. Hellman–Feynman force constants are reasonable but poor for the diagonal harmonic terms. Again a surprisingly good agreement for the cubic stretching force constants is found. The quasi-

TABLE X. Components of force constants for third period hydrides.[a]

Force constant	V_{NE}(opr)	V_{NE}(wfn)	Kinetic	V_{EE}	Coefficient	Nuclear	Total	Hellmann–Feynman
					Components[b]			
HCl								
f_{rr}	-28.38813	-38.77062	5.90352	26.61099	1.91869	38.01492	5.28937	9.62679
f_{rrr}	74.78308	25.53329	-13.93902	-25.81404	-0.48829	-89.44296	-29.36795	-14.65988
H₂S								
f_{rr}	-23.16774	-22.15040	4.12365	14.34012	0.88265	29.93030	3.95859	6.76256
$f_{rr'}$	-1.80960	-2.22804	0.14140	3.37515	0.06387	0.44024	-0.01698	-1.34926
$f_{\theta\theta}$	3.20797	17.87107	-0.98916	-18.69948	-1.20916	0.75677	0.93802	2.45120
f_{rrr}	54.23211	3.01051	-8.84668	-4.97408	1.49596	-65.74215	-20.82433	-11.51004
PH₃								
f_{rr}	19.09976	-9.45071	2.29304	5.29861	0.16058	23.87365	3.07542	4.77390
$f_{rr'}$	-1.01398	-0.61616	0.03385	1.32682	-0.11067	0.37723	-0.00289	-0.63675
$f_{\theta\theta}$	-2.62734	18.45901	-0.97333	-18.79757	-1.16779	0.73173	0.87940	1.89561
$f_{\theta\theta'}$	0.74584	-1.84461	0.03235	0.95941	0.06990	0.0	-0.03712	0.74584
f_{rrr}	40.88130	2.55543	-6.07609	-3.63119	1.54145	-49.15749	-13.88658	-8.27619
SiH₄								
f_{rr}	-16.47414	-5.50723	1.48125	3.29537	-0.32881	20.46228	2.92871	3.98814
$f_{rr'}$	-0.26422	0.47073	-0.05311	-0.24459	-0.14276	0.27216	0.03822	0.00794
f_{rrr}	28.18926	-22.82608	-0.17217	19.40208	3.54547	-40.63497	-12.49641	-12.44571

[a]Units: See Tables I and II.
[b]As defined by Eq. (2.3) and calculated with the 4-31G basis set.

virial relationship noted for bending motions in the second period hydrides is also found for the third period hydrides.

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