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Self-Consistent Molecular-Orbital Methods. 22. Small Split-Valence Basis Sets for Second-Row Elements

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Abstract: Two new split-valence basis sets, termed 6-21G and 3-21G, recently proposed for use in molecular orbital calculations on molecules containing first-row elements have been extended through the second row. The valence functions for the smaller representation (3-21G) have been taken directly from the larger (6-21G), preventing their collapse inwards to make up for deficiencies in the inner-shell region. This is necessary to ensure a good description of bonding interactions which necessarily involve overlap of valence functions. Equilibrium geometries, vibrational frequencies, relative energies, and electric dipole moments calculated with the use of the 3-21G basis set for a number of molecules containing second-row atoms are nearly identical with those obtained from the larger 6-21G representation. Compared to experiment they are consistently superior to properties derived from the STO-3G minimal basis set, and of comparable quality to those obtained from the larger 4-31G split-valence representation. The 3-21G basis set comprises the same number of primitive Gaussian functions as STO-3G (although a significantly greater number of basis functions), and should be nearly as efficient computationally as that representation for applications which require evaluation of energy derivatives as well as the energy itself (e.g., determination of equilibrium geometry and calculation of vibrational frequencies). It is significantly less costly to apply than the 4-31G basis set, and would appear to be the method of choice for split-valence level Hartree–Fock calculations on moderately sized molecules.

In a recent paper[2] we proposed two new series of computationally efficient split-valence basis sets for use in molecular orbital calculations on molecules containing first-row elements. The larger of the two, termed 6-21G, utilizes six Gaussian functions for its inner (1s) shell, and has two valence shells (2s, 2p) comprising two and one Gaussian functions, respectively. It has been constructed much in the same way as the previously introduced 4-31G and 6-31G split-valence basis sets,[3] by optimization of all Gaussian exponents and contraction coefficients so as to give the lowest spin unrestricted Hartree–Fock energy for the ground state of the atom. In previous work difficulties were encountered when this procedure was followed, using a small number of Gaussians to represent inner-shell functions. For atoms with few valence electrons (e.g., lithium and beryllium) there is a tendency for the valence functions to "fall inwards" toward the nucleus, because the total energy minimization criterion prefers to have additional functions in the inner-shell region rather than providing a good description of the valence region. In fact, suitable 4-31G basis sets for lithium and beryllium could not be found, and 5-21G basis representations were eventually introduced as substitutes.[3e] This tendency to "fall inward" is not a problem with the 6-21G basis sets where the description of the inner shell is adequate. It is a problem for the smaller of the new representations, termed 3-21G (inner-shell basis function written as a linear combination of three Gaussian primitives; valence functions split into two and one Gaussian parts), and the valence basis functions here have been constrained to be identical with those in the corresponding 6-21G sets (i.e., only the inner-shell exponents and contraction coefficients have been optimized). Such a procedure effectively prevents the collapse of the valence functions into the inner shell and, therefore, ensures adequate description of bonding interactions which involve overlap of valence functions.

The performance of the 6-21G and 3-21G split-valence basis sets for first-row elements has been thoroughly assessed with regard to the calculation of equilibrium geometries and molecular vibrational frequencies and the description of relative molecular energies and electric dipole moments. The major points that have been made are: (i) that for all properties considered (excepting total energy) the results of the 6-21G and 3-21G basis sets are nearly identical, (ii) that equilibrium geometries calculated with the use of the 6-21G and 3-21G basis sets are (in the mean) superior to those obtained from minimal basis set STO-3G calculations,[4] and of approximately equal quality to 4-31G level structures, (iii) that vibrational frequencies obtained with the use of either of the 6-21G or 3-21G basis sets are also of comparable quality if not superior to those derived from 4-31G, and significantly closer to experiment than STO-3G values, (iv) that although the 6-21G and 3-21G basis sets do not fare as well as 4-31G with regard to the calculation of the energetics of complete hydrogenation, calculated 6-21G and 3-21G relative isomer energies are of comparable quality to those obtained at the 4-31G level, and provide significantly better descriptions of relative energies than STO-3G, and finally (v) that 6-21G and 3-21G electric dipole moments are, in the mean, closer to experimental values than those obtained either from 4-31G (which are generally larger) or from STO-3G (which are generally smaller).

The 3-21G basis sets contains fewer primitive Gaussian functions than the previously introduced and widely employed 4-31G representation and, therefore, offers significant computational advantage particularly in applications which call for evaluation of energy derivatives as well as the energy itself (e.g., geometry optimization and force constant evaluation). It contains the same number of primitives as the widely used STO-3G basis set, although it comprises almost twice the number of basis functions per atom (2 for hydrogen and helium and 9 for lithium to neon vs. 1 and 5 basis functions respectively for the minimal set). Therefore, 3-21G calculations which are heavily dominated by the integral evaluation steps required for derivative evaluation should be only slightly higher in cost than those at the minimal basis set STO-3G level, while "single-point" 3-21G calculations, which are often dominated by the SCF procedure (which depends directly only on the number of basis functions and not on their makeup), will be significantly (ca. factor of 2) more costly. Because of its increased number of basis functions (but not of primitive Gaussians) the range of application of the 3-21G basis set may be more limited than STO-3G. Where size limitations do not restrict its use, our work thus far has indicated it to be a

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Table I. 6-21G Basis Functions for Sodium to Argon

atom	α_1	d_{1s}	α_2	d_{2s}	d_{2p}	α_3'	d_{3s}'	d_{3p}'	α_3''
Na	9.99320 (+3)	1.93766 (−3)	1.50963 (+2)	−3.54208 (−3)	5.00166 (−3)	5.01824 (−1)	−2.19660 (−1)	9.06649 (−3)	2.44349 (−2)
	1.49989 (+3)	1.48070 (−2)	3.55878 (+1)	−4.39588 (−2)	3.55109 (−2)	6.09458 (−2)	1.08912	9.97202 (−1)	
	3.41951 (+2)	7.27055 (−2)	1.11683 (+1)	−1.09752 (−1)	1.42825 (−1)				
	9.46796 (+1)	2.52629 (−1)	3.90201	1.87398 (−1)	3.38620 (−1)				
	2.97345 (+1)	4.93242 (−1)	1.38177	6.46699 (−1)	4.51579 (−1)				
	1.00063 (+1)	3.13169 (−1)	4.66382 (−1)	3.06058 (−1)	2.73271 (−1)				
Mg	1.17228 (+4)	1.97783 (−3)	1.89180 (+2)	−3.23717 (−3)	4.92813 (−3)	6.11349 (−1)	−3.61101 (−1)	2.42633 (−2)	4.64011 (−2)
	1.75993 (+3)	1.51140 (−2)	4.52119 (+1)	−4.10079 (−2)	3.49888 (−2)	1.41841 (−1)	1.21505	9.86673 (−1)	
	4.00846 (+2)	7.39108 (−2)	1.43563 (+1)	−1.12600 (−1)	1.40725 (−1)				
	1.12807 (+2)	2.49191 (−1)	5.13886	1.48633 (−1)	3.33642 (−1)				
	3.59997 (+1)	4.87928 (−1)	1.90652	6.16497 (−1)	4.44940 (−1)				
	1.21828 (+1)	3.19662 (−1)	7.05887 (−1)	3.64829 (−1)	2.69254 (−1)				
Al	1.39831 (+4)	1.94267 (−3)	2.39668 (+2)	−2.92619 (−3)	4.60285 (−3)	9.46160 (−1)	−3.20327 (−1)	5.19383 (−2)	6.39088 (−2)
	2.09875 (+3)	1.48599 (−2)	5.74419 (+1)	−3.74083 (−2)	3.31990 (−2)	2.02506 (−1)	1.18412	9.72660 (−1)	
	4.77705 (+2)	7.28494 (−2)	1.82859 (+1)	−1.14487 (−1)	1.36282 (−1)				
	1.34360 (+2)	2.46830 (−1)	6.59914	1.15635 (−1)	3.30476 (−1)				
	4.28709 (+1)	4.87258 (−1)	2.49049	6.12595 (−1)	4.49146 (−1)				
	1.45189 (+1)	3.23496 (−1)	9.44545 (−1)	3.93799 (−1)	2.65704 (−1)				
Si	1.61159 (+4)	1.95948 (−3)	2.92718 (+2)	−2.78094 (−3)	4.43826 (−3)	1.07913	−3.76108 (−1)	6.71030 (−2)	9.33392 (−2)
	2.42558 (+3)	1.49288 (−2)	6.98731 (+1)	−3.57146 (−2)	3.26679 (−2)	3.02422 (−1)	1.25165	9.56883 (−1)	
	5.53867 (+2)	7.28478 (−2)	2.23363 (+1)	−1.14985 (−1)	1.34721 (−1)				
	1.56340 (+2)	2.46130 (−1)	8.15039	9.35634 (−2)	3.28678 (−1)				
	5.00683 (+1)	4.85914 (−1)	3.13458	6.03017 (−1)	4.49640 (−1)				
	1.70178 (+1)	3.25002 (−1)	1.22543	4.18959 (−1)	2.61372 (−1)				
P	1.94133 (+4)	1.85160 (−3)	3.39478 (+2)	−2.78217 (−3)	4.56462 (−3)	1.21865	−3.71495 (−1)	9.15823 (−2)	1.22811 (−1)
	2.90942 (+3)	1.42062 (−2)	8.10101 (+1)	−3.60499 (−2)	3.36936 (−2)	3.95546 (−1)	1.27099	9.34924 (−1)	
	6.61364 (+2)	6.99995 (−2)	2.58780 (+1)	−1.16631 (−1)	1.39755 (−1)				
	1.85759 (+2)	2.40079 (−1)	9.45221	9.68328 (−2)	3.39362 (−1)				
	5.91943 (+1)	4.84762 (−1)	3.66566	6.14418 (−1)	4.50921 (−1)				
	2.00310 (+1)	3.35200 (−1)	1.46746	4.03798 (−1)	2.38586 (−1)				
S	2.19171 (+4)	1.86924 (−3)	4.23735 (+2)	−2.37677 (−3)	4.06101 (−3)	1.22384	−2.86089 (−1)	1.64777 (−1)	1.42269 (−1)
	3.30149 (+3)	1.42303 (−2)	1.00710 (+2)	−3.16930 (−2)	3.06813 (−2)	4.57303 (−1)	1.22806	8.70855 (−1)	
	7.54146 (+2)	6.96962 (−2)	3.21599 (+1)	−1.13317 (−1)	1.30452 (−1)				
	2.12711 (+2)	2.38487 (−1)	1.18079 (+1)	5.60900 (−2)	3.27205 (−1)				
	6.79896 (+1)	4.83307 (−1)	4.63110	5.92255 (−1)	4.52851 (−1)				
	2.30515 (+1)	3.38074 (−1)	1.87025	4.55006 (−1)	2.56042 (−1)				
Cl	2.51801 (+4)	1.83296 (−3)	4.91765 (+2)	−2.29739 (−3)	3.98940 (−3)	1.35299	−2.22401 (−1)	2.19216 (−1)	1.66714 (−1)
	3.78035 (+3)	1.40342 (−2)	1.16984 (+2)	−3.07137 (−2)	3.03177 (−2)	5.26955 (−1)	1.18252	8.22321 (−1)	
	8.60474 (+2)	6.90974 (−2)	3.74153 (+1)	−1.12528 (−1)	1.29880 (−1)				
	2.42145 (+2)	2.37452 (−1)	1.37834 (+1)	4.50163 (−2)	3.27951 (−1)				
	7.73349 (+1)	4.83034 (−1)	5.45215	5.89353 (−1)	4.53527 (−1)				
	2.62470 (+1)	3.39856 (−1)	2.22588	4.65206 (−1)	2.52154 (−1)				
Ar	2.83483 (+4)	1.82526 (−3)	5.75891 (+2)	−2.15972 (−3)	3.80665 (−3)	1.54209	−1.76866 (−1)	2.55687 (−1)	1.95373 (−1)
	4.25762 (+3)	1.39686 (−2)	1.36816 (+2)	−2.90775 (−2)	2.92305 (−2)	6.07267 (−1)	1.14690	7.89842 (−1)	
	9.69857 (+2)	6.87073 (−2)	4.38098 (+1)	−1.10827 (−1)	1.26467 (−1)				
	2.73263 (+2)	2.36204 (−1)	1.62094 (+1)	2.76999 (−2)	3.23510 (−1)				
	8.73695 (+1)	4.82214 (−1)	6.46084	5.77613 (−1)	4.54896 (−1)				
	2.96867 (+1)	3.42043 (−1)	2.65114	4.88688 (−1)	2.56630 (−1)				

Table II. 3-21G Inner-Shell Basis Functions for Sodium to Argon

atom	α_1	d_{1s}	α_2	d_{2s}	d_{2p}
Na	5.47613 (+2)	6.74911 (−2)	1.75407 (+1)	−1.11937 (−1)	1.28233 (−1)
	8.20678 (+1)	3.93505 (−1)	3.79398	2.54654 (−1)	4.71533 (−1)
	1.76917 (+1)	6.65605 (−1)	9.06441 (−1)	8.44417 (−1)	6.04273 (−1)
Mg	6.52841 (+2)	6.75982 (−2)	2.33727 (+1)	−1.10246 (−1)	1.21014 (−1)
	9.83805 (+1)	3.91778 (−1)	5.19953	1.84119 (−1)	4.62810 (−1)
	2.12996 (+1)	6.66661 (−1)	1.31508	8.96399 (−1)	6.06907 (−1)
Al	7.75737 (+2)	6.68347 (−2)	2.94796 (+1)	−1.07902 (−1)	1.17574 (−1)
	1.16952 (+2)	3.89061 (−1)	6.63314	1.46245 (−1)	4.61174 (−1)
	2.53326 (+1)	6.69468 (−1)	1.72675	9.23730 (−1)	6.05535 (−1)
Si	9.10655 (+2)	6.60823 (−2)	3.66716 (+1)	−1.04511 (−1)	1.13355 (−1)
	1.37336 (+2)	3.86229 (−1)	8.31729	1.07410 (−1)	4.57578 (−1)
	2.97601 (+1)	6.72380 (−1)	2.21645	9.51446 (−1)	6.07427 (−1)
P	1.05490 (+3)	6.55407 (−2)	4.42866 (+1)	−1.02130 (−1)	1.10851 (−1)
	1.59195 (+2)	3.84036 (−1)	1.01019 (+1)	8.15922 (−2)	4.56495 (−1)
	3.45304 (+1)	6.74541 (−1)	2.73997	9.69788 (−1)	6.06936 (−1)
S	1.21062 (+3)	6.50071 (−2)	5.22236 (+1)	−1.00310 (−1)	1.09646 (−1)
	1.82747 (+2)	3.82040 (−1)	1.19629 (+1)	6.50877 (−2)	4.57649 (−1)
	3.96673 (+1)	6.76545 (−1)	3.28911	9.81455 (−1)	6.04261 (−1)
Cl	1.37640 (+3)	6.45827 (−2)	6.08014 (+1)	−9.87639 (−2)	1.08598 (−1)
	2.07857 (+2)	3.80363 (−1)	1.39765 (+1)	5.11338 (−2)	4.58682 (−1)
	4.51554 (+1)	6.78190 (−1)	3.88710	9.91337 (−1)	6.01962 (−1)
Ar	1.55371 (+3)	6.41707 (−2)	7.00453 (+1)	−9.74661 (−2)	1.07619 (−1)
	2.34678 (+2)	3.78797 (−1)	1.61473 (+1)	3.90569 (−2)	4.59576 (−1)
	5.10121 (+1)	6.79752 (−1)	4.53492	9.99916 (−1)	6.00041 (−1)

reasonable alternative to both STO-3G and 4-31G as a general tool for the investigation of molecular structure.

In this paper we present the extension of our work on the 6-21G and 3-21G split-valence basis sets to second-row elements. Second-row split-valence representations defined previously include the 4-31G (44-31G) basis set.[3c] This was originally formulated only for the elements phosphorus, sulfur, and chlorine, as attempts to obtain representations for elements on the left-hand side of the row proved unsuccessful due to partial collapse of the valence functions into the inner shell. Therefore, computations on molecules containing the second-row elements sodium, magnesium, aluminum, and silicon of comparable quality to first-row 4-31G calculations have not hitherto been possible. In addition, definition of a 4-31G basis set for argon was never attempted. Paralleling our work on the first row, we have developed 33-21G (3-21G in short) representations for second-row atoms via a three-step procedure. The first stage has been to seek optimum 66-21G (6-21G for short) basis sets. Then holding the valence functions (3s, 3p) fixed so as to prohibit their collapse into the inner-shell region, inner shells have been redetermined with the use of a 63 contraction (six Gaussians to describe the 1s basis functions; 3 each to describe the 2s and 2p functions). Finally, while holding both inner-shell (2s, 2p) and valence-shell (3s, 3p) functions constant, the 1s basis function has been reoptimized at a contraction level of three.

Atomic Basis Sets

Basis functions for Na to Ar are defined in the following manner,

$$
\begin{aligned}
\varphi_{1s}(\mathrm{r}) &= \sum_{k=1}^{K} d_{1s,k}g_s(\alpha_{1,k},\mathrm{r}) \\
\varphi_{2s}(\mathrm{r}) &= \sum_{k=1}^{L} d_{2s,k}g_s(\alpha_{2,k},\mathrm{r}) \\
\varphi_{2p}(\mathrm{r}) &= \sum_{k=1}^{L} d_{2p,k}g_p(\alpha_{2,k},\mathrm{r}) \\
\varphi_{3s}'(\mathrm{r}) &= \sum_{k=1}^{2} d'_{3s,k}g_s(\alpha'_{3,k},\mathrm{r}) \\
\varphi_{3p}'(\mathrm{r}) &= \sum_{k=1}^{2} d'_{3p,k}g_p(\alpha'_{3,k},\mathrm{r}) \\
\varphi_{3s}''(\mathrm{r}) &= g_s(\alpha''_3,\mathrm{r}) \\
\varphi_{3p}''(\mathrm{r}) &= g_p(\alpha''_3,\mathrm{r})
\end{aligned}
\qquad (1)
$$

where g_s and g_p are normalized s- and p-type Gaussian functions, respectively. The 6-21G and 3-21G basis sets introduced in this paper have $K = L = 6$ and $K = L = 3$, respectively. The intermediate 63-21G basis set is defined by $K = 6$, $L = 3$.

6-21G basis functions are obtained by minimization of the UHF atomic energies,[5] all d coefficients and α exponents in expression

Table III. Ground State Energies of Second-Row Atoms (hartrees), 6-21G and 3-21G Basis Sets

atom (electronic state)	E(6-21G)	E(3-21G)
Na (^{2}S)	−161.84138	−160.85407
Mg[a] (^{1}S)	−199.59492	−198.46810
Al (^{2}P)	−241.85265	−240.55105
Si (^{3}P)	−288.82539	−287.34443
P (^{4}S)	−340.68408	−339.00008
S (^{3}P)	−397.46372	−395.55134
Cl ($^2_2$P)	−459.43318	−457.27655
Ar (^{1}S)	−526.75041	−524.34296

[a] ^{3}P excited state energies: 6-21G, −199.52675 hartrees; 3-21G, −198.40070 hartrees.

Table IV. Calculated and Experimental Equilibrium Geometries for One-Heavy-Atom Hydrides

molecule	point group	geometrical parameter	6-21G	3-21G	STO-3G	4-31G	exptl
NaH[a]	$C_{\infty v}$	r(NaH)	1.909	1.926	1.654		1.887
MgH_2	$D_{\infty h}$	r(MgH)	1.722	1.726	1.542		
AlH_3	D_{3h}	r(AlH)	1.601	1.599	1.476		
SiH_4[b]	T_d	r(SiH)	1.489	1.487	1.422		1.481
PH_3[b]	C_{3v}	r(PH)	1.423	1.423	1.378	1.433	1.420
		∠(HPH)	96.4	96.1	95.0	95.0	93.3
H_2S[b]	C_{2v}	r(SH)	1.351	1.350	1.329	1.354	1.336
		∠(HSH)	96.1	95.8	92.5	95.5	92.1
HCl[a]	$C_{\infty v}$	r(ClH)	1.294	1.293	1.313	1.299	1.275

[a] Experimental data from: D. R. Stull and J. Prophet, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971). [b] Experimental data from: J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Lafferty, A. G. Maki, and C. S. Pote, "Structure Data on Free Polyatomic Molecules", Landolt-Börnstein, New Series, Group II, Vol. 7, K. H. Hellwege and A. M. Hellwege, Eds, Springer-Verlag, Berlin, 1976.

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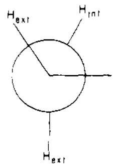
(6) All molecular calculations have been carried out with the use of the GAUSSIAN-82 program on Harris Corporation Slash 6 and H100 digital computers.

Table V. Calculated and Experimental Equilibrium Geometries for Two-Heavy-Atom Hydrides

molecule	point group	geometrical parameter[f]	6-21G	3-21G	STO-3G	4-31G	exptl
LiCl[a]	$C_{\infty v}$	$r(\mathrm{LiCl})$	2.106	2.112	1.933	2.075	2.021
CH_3SiH_3[b]	C_{3v}	$r(\mathrm{CSi})$	1.913	1.917	1.861		1.867
		$r(\mathrm{CH})$	1.085	1.085	1.082		1.093
		$r(\mathrm{SiH})$	1.493	1.490	1.423		1.485
		$\angle(\mathrm{HCH})$	108.2	108.3	107.6		107.7
		$\angle(\mathrm{HSiH})$	108.2	108.3	108.8		108.3
HCP[b]	$C_{\infty v}$	$r(\mathrm{CP})$	1.549	1.548	1.472	1.535	1.540
		$r(\mathrm{CH})$	1.059	1.057	1.069	1.056	1.069
H_2CPH[c]	C_s	$r(\mathrm{CP})$	1.686	1.683	1.615	1.672	1.67
		$r(\mathrm{CH_{anti}})$	1.073	1.073	1.081	1.072	
		$r(\mathrm{CH_{syn}})$	1.073	1.073	1.080	1.071	
		$r(\mathrm{PH})$	1.434	1.433	1.390	1.449	
		$\angle(\mathrm{H_{anti}CP})$	119.6	119.5	120.7	119.7	
		$\angle(\mathrm{H_{syn}CP})$	124.7	124.7	126.3	125.2	
		$\angle(\mathrm{HPC})$	98.7	98.8	97.0	98.4	
CH_3PH_2[b,d]	C_s	$r(\mathrm{CP})$	1.910	1.908	1.841	1.916	1.862
		$r(\mathrm{CH_{tr}})$	1.081	1.081	1.084	1.078	1.094
		$r(\mathrm{CH_g})$	1.082	1.082	1.083	1.080	1.094
		$r(\mathrm{PH})$	1.426	1.425	1.381	1.435	1.432
		$\angle(\mathrm{PHC_{tr}})$	112.3	112.1	113.1	112.1	109.2
		$\angle(\mathrm{PCH_gH_{g'}})$	123.2	123.5	125.7	122.9	
		$\angle(\mathrm{H_gCH_{g'}})$	108.6	108.9	107.4	108.6	
		$\angle(\mathrm{CPHH})$	102.6	101.8	98.9	101.0	
		$\angle(\mathrm{HPH})$	96.0	95.6	93.7	94.6	
CS[a]	$C_{\infty v}$	$r(\mathrm{CS})$	1.566	1.564	1.519	1.555	1.535
H_2CS[b]	C_{2v}	$r(\mathrm{CS})$	1.639	1.638	1.574	1.630	1.611
		$r(\mathrm{CH})$	1.074	1.073	1.090	1.072	1.093
		$\angle(\mathrm{HCH})$	116.5	116.5	112.0	115.5	116.9
CH_3SH[b,e]	C_s	$r(\mathrm{CS})$	1.891	1.895	1.798	1.887	1.819
		$r(\mathrm{CH_{tr}})$	1.078	1.078	1.085	1.076	1.091
		$r(\mathrm{CH_g})$	1.078	1.077	1.087	1.076	1.091
		$r(\mathrm{SH})$	1.353	1.352	1.331	1.357	1.336
		$\angle(\mathrm{SCH_{tr}})$	105.7	105.6	108.5	105.7	
		$\angle(\mathrm{SCH_gH_{g'}})$	126.9	126.6	130.1	127.5	
		$\angle(\mathrm{H_gCH_{g'}})$	111.2	111.4	108.1	111.0	109.8
		$\angle(\mathrm{CSH})$	98.1	97.9	95.4	97.9	96.5
CH_3Cl[b]	C_{3v}	$r(\mathrm{CCl})$	1.884	1.892	1.802	1.881	1.781
		$r(\mathrm{CH})$	1.074	1.073	1.088	1.072	1.096
		$\angle(\mathrm{HCH})$	112.3	112.6	110.1	112.1	110.0
PN	$C_{\infty v}$	$r(\mathrm{PN})$	1.513	1.510	1.459	1.493	1.491
HPO[b]	C_s	$r(\mathrm{PO})$	1.549	1.544	1.515	1.540	1.512
		$r(\mathrm{PH})$	1.448	1.447	1.410	1.477	
		$\angle(\mathrm{HOCl})$	103.5	103.5	99.1	101.2	104.7
HOCl[b]	C_s	$r(\mathrm{OCl})$	1.765	1.767	1.737	1.876	1.690
		$r(\mathrm{OH})$	0.977	0.975	1.004	0.959	0.975
		$\angle(\mathrm{HOCl})$	101.7	104.2	100.2	105.4	102.5
NaOH[a]	$C_{\infty v}$	$r(\mathrm{NaO})$	1.868	1.870	1.763		1.95
		$r(\mathrm{OH})$	0.963	0.962	0.988		0.96
NaF[a]	$C_{\infty v}$	$r(\mathrm{NaF})$	1.865	1.863	1.753		1.926
SiO[a]	$C_{\infty v}$	$r(\mathrm{SiO})$	1.538	1.536	1.475		1.509
SiH_3F[b]	C_{3v}	$r(\mathrm{SiF})$	1.639	1.635	1.624		1.596
		$r(\mathrm{SiH})$	1.481	1.478	1.422		1.480
		$\angle(\mathrm{HSiH})$	109.7	109.8	109.6		110.6
ClF[a]	$C_{\infty v}$	$r(\mathrm{ClF})$	1.691	1.689	1.677	1.714	1.628
Na_2[a]	$C_{\infty h}$	$r(\mathrm{NaNa})$	3.199	3.228	2.359		3.078
NaCl[a]	$C_{\infty v}$	$r(\mathrm{NaCl})$	2.424	2.421	2.221		2.361
SiH_3SiH_3[b]	D_{3d}	$r(\mathrm{SiSi})$	2.379	2.382	2.243		1.327
		$r(\mathrm{SiH})$	1.490	1.488	1.423		1.486
		$\angle(\mathrm{HSiH})$	108.8	108.8	108.0		107.9
SiH_3Cl[b]	C_{3v}	$r(\mathrm{SiCl})$	2.187	2.191	2.089		2.048
		$r(\mathrm{SiH})$	1.477	1.475	1.423		1.483
		$r(\mathrm{HSiH})$	111.6	111.8	111.2		110.2
P_2[a]	$D_{\infty h}$	$r(\mathrm{PP})$	1.927	1.930	1.808	1.914	1.894
P_2H_4[b,g]	C_2	$r(\mathrm{PP})$	2.339	2.356	2.175	2.354	2.219
		$r(\mathrm{PH_{int}})$	1.422	1.419	1.379	1.432	1.417
		$r(\mathrm{PH_{ext}})$	1.420	1.419	1.380	1.435	1.414
		$\angle(\mathrm{PPH_{int}})$	99.9	99.1	96.2	95.2	99.1
		$\angle(\mathrm{PPH_{ext}})$	96.1	95.5	96.9	98.4	94.3
		$\angle(\mathrm{H_{int}PH_{ext}})$	96.1	95.8	94.1	94.9	92.0
		$\omega(\mathrm{H_{int}PPH_{ext}})$	79.1	79.1	79.1	79.3	74.0
HSSH[b]	C_2	$r(\mathrm{SS})$	2.246	2.264	2.065	2.243	2.055
		$r(\mathrm{SH})$	1.352	1.352	1.334	1.356	1.327
		$\angle(\mathrm{SSH})$	97.3	96.7	96.9	96.8	91.3
		$\omega(\mathrm{HSSH})$	93.9	93.7	92.6	95.4	90.6
Cl_2[a]	$D_{\infty h}$	$r(\mathrm{ClCl})$	2.178	2.193	2.063	2.177	1.988

Table V (*footnotes*)

[a] See footnote *a* of Table IV for reference to experimental data. [b] See footnote *b* of Table IV for reference to experimental data. [c] C=P bond length estimated from investigations on CH_2=PCl, CF_2=PH, and CH_2=PH. M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. E. Simmons, *J. Chem. Soc., Chem. Commun.*, 513 (1976). [d] Subscripts tr, g, and g' refer to relative orientations of the phosphorus lone pair to CH bonds of 180 and ±60°, respectively, $PCH_gH_{g'}$ refers to the angle between the PC bond and the line bisecting the $H_gCH_{g'}$ plane. CPHH refers to the angle between the CP bond and the line bisecting the HPH plane. [e] Subscripts tr, g, and g' refer to relative orientations of SH and CH bonds of 180 and ±60°, respectively. $SCH_gH_{g'}$ refers to the angle between the SC bond and the line bisecting the $H_gH_{g'}$ plane. [f] *r* in Å and angles in deg. [g] Subscripts int and ext refer to the projection below:



1 being independently varied subject to overall normalization. Details of the minimization procedure have been dealt with elsewhere.[3a] The atomic ground state is used for all atoms except sodium and magnesium. For the latter the $(1s)^2(2s)^2(2p)^6(3s)(3p)$ ^3P excited state is used to obtain a reasonable simultaneous description of the valence s- and p-type orbitals. For sodium, the valence s-type basis functions are determined by using the $(1s)^2(2s)^2(2p)^6(3s)$ ^2S ground state with a basis set lacking 3p-type functions. Subsequent to this, valence 3p functions are added and their contraction coefficients determined by using the $(1s)^2(2s)^2(2p)^6(3p)$ ^2P excited state holding all exponents and all other contraction coefficients fixed. A complete listing of exponents and contraction coefficients is given in Table I.

As indicated in the introduction, 3-21G basis functions for second-row atoms may not be obtained directly from the 6-21G sets; rather intermediate 63-21G basis sets must first be constructed. This is done by holding the Gaussian exponents and contraction coefficients of the two valence shells (3sp′, 3sp″) fixed (at the values appropriate to the 6-21G expansions) and reoptimizing the inner 1s and 2sp shells at contraction levels of 6 and 3 Gaussians, respectively. Again minimization is carried out for the atomic ground states with the previously mentioned exceptions of sodium and magnesium. 3-21G basis sets are then constructed from the 63-21G representations by energy minimization subject to constraining all basis functions except the innermost 1s shell. This roundabout optimization procedure ensures that the valence-shells (3sp′, 3sp″) of the 3-21G basis sets will not act to supplement insufficient inner-shell descriptions. Rather, their construction against the backdrop of flexible (six Gaussian) inner-shell representations guarantees that they will be appropriate for description of bonding. Inner-shell (1s, 2sp) functions for 3-21G basis sets for sodium to argon are given in Table II (the valence parts are to be found in Table I). 6-21G and 3-21G atom ground state energies are presented in Table III.

Paralleling the procedure followed for first-row 6-21G and 3-21G basis sets (but not for the 21G hydrogen representation), the tabulated functions are to be employed directly without scaling for calculations on molecules. In our previous work on the first row it was found that, with the exception of hydrogen, optimum scale factors for atoms in molecules both less and greater than unity were commonplace. It was therefore decided that the unscaled atomic basis sets were as legitimate a choice as any scaled sets for molecular calculations.

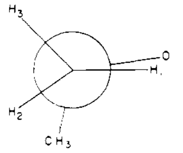
Performance of the 6-21G and 3-21G Split-Valence Basis Sets[6]

Equilibrium Geometry Comparisons. Equilibrium geometries calculated for the one-heavy-atom hydrides of sodium to chlorine using the 6-21G and 3-21G basis sets are presented in Table IV. They are compared both with the experimental geometries where available and with the results of calculations at the minimal STO-3G and split-valence 4-31G levels (PH_3, H_2S, and HCl only).

Table VI. Calculated and Experimental Equilibrium Geometries of Hypervalent Molecules

molecule	point point	geometrical parameter[b]	STO-3G	STO-3G*	3-21G	exptl[a]
F_3PO	C_{3v}	*r*(PO)	1.557	1.431	1.506	1.436
		r(PF)	1.612	1.523	1.575	1.524
		∠(FPF)	98.9	100.5	100.0	101.3
$(CH_3)_2SO$	C_s[c]	*r*(SO)	1.820	1.480	1.678	1.485
		r(SC)	1.809	1.818	1.862	1.799
		r(CH_1)	1.086	1.088	1.079	1.054
		r(CH_2)	1.086	1.087	1.078	1.097
		r(CH_3)	1.085	1.087	1.078	1.093
		∠(CSC)	98.4	94.8	98.1	96.6
		∠(OSC)	103.6	107.8	105.0	106.7
		∠(SCH_1)	110.6	110.9	108.0	108.3
		∠(SCH_2)	110.7	110.4	109.2	108.2
		∠(SCH_3)	108.3	107.8	106.7	109.6
		∠(H_1CH_2)	109.0	109.0	112.0	113.6
		∠(H_1CH_3)	108.7	109.0	109.8	110.6
		ω(H_2CSO)	43.6	51.8	48.0	
ClF_3	C_{2v}	*r*(ClF_{eq})	1.787	1.650	1.757	1.598
		r(ClF_{ax})	1.791	1.662	1.671	1.698
		∠(F_{eq}-ClF_{ax})	77.8	83.7	83.7	87.5

[a] See footnote *b* of Table IV for reference to experimental data. [b] *r* in Å and angles in deg. [c] Subscripts on hydrogens refer to the projection below



The performance of all three split-valence basis sets is remarkably similar. Overall, 6-21G and 3-21G level bond lengths (which generally are nearly identical) are in slightly better accord with experimental values than those calculated with the use of the 4-31G representation; on the other hand, 4-31G bond angles (in phosphine and hydrogen sulfide) are marginally the superior. With the exception of H_2S, experimental bond lengths in the second-row hydrides are better described by using any of the split-valence basis sets (all of which generally overestimate bond distances) than by use of STO-3G (which usually yields lengths which are too short). For both PH_3 and H_2S the STO-3G basis set provides the best description of equilibrium bond angles.

A comparison of theoretical (6-21G, 3-21G, STO-3G, and 4-31G levels) and experimental equilibrium structures for a larger set of two-heavy-atom hydrides is found in Table V. As in the previous comparison (Table IV), and in those involving first-row elements only,[2] structures calculated at the 6-21G and 3-21G levels are in nearly perfect accord with one another. In addition, they are qualitatively similar to those derived from the 4-31G basis set. Calculated 6-21G and 3-21G single bond lengths between heavy (non-hydrogen) atoms are consistently longer than the corresponding experimental values, deviations being most significant for the PP bond in P_2H_4, the SS linkage in H_2S_2, and the CS and CCl bonds in methane thiol and methyl chloride, re-

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(7) D. J. DeFrees, B. A. Levi, S. K. Pollack, E. S. Blurock, R. F. Hout, Jr., W. J. Pietro, M. M. Francl, and W. J. Hehre, to be submitted to Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.

Table VII. Calculated and Experimental Vibration Frequencies (cm^{-1})

molecule	vibrational mode	6-21G// 6-21G^a	3-21G// 3-21G^a	STO-3G// STO-3G^a	4-31G// 4-31G^a	exptl^b
H_2S	symmetric stretch	2661	2642	3273	2602	2615
	bend	1308	1323	1612	1329	1183
	asymmetric stretch	2676	2656	3323	2620	2626
PH_3	symmetric stretch	2416	2404	3040	2286	2323
	bend	1087	1093	1428	1115	992
	degenerate stretch	2417	2398	3092	2307	2328
	degenerate bend	1258	1271	1564	1274	1118

[a] See footnote *a* of Table VII. [b] Experimental frequencies from: T. Shimanouchi, *Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 39 (1972).

Table VIII. Calcualted Total Energies (hartrees)

molecule	6-21G// 6-21G^a	3-21G// 3-21G^a	STO-3G// STO-3G^a	4-31G// 4-31G^a
NaH	−162.36834	−161.38118	−160.31570	
MgH_2	−200.70603	−199.58136	−198.21938	
AlH_3	−243.58264	−242.28411	−240.72842	
SiH_4	−291.16666	−289.68698	−287.91728	
PH_3	−342.38710	−340.70452	−338.63641	−342.02557
H_2S	−398.61606	−396.70467	−394.31163	−398.20395
HCl	−460.02531	−457.86943	−455.13601	−459.56342
LiCl	−466.99086	−464.79062	−461.99236	−466.52693
CH_3SiH_3	−330.17574	−328.52612	−326.51106	
HCP	−379.02557	−377.17103	−374.80066	−378.64417
H_2CPH	−380.19632	−378.34114	−375.98852	−379.81575
CH_3PH_2	−381.38723	−379.53373	−377.22386	−381.01277
CH_3SH	−437.60918	−435.52629	−432.89535	−437.18298
H_2CS	−436.42129	−434.33625	−431.65479	−435.99188
CH_3Cl	−499.01711	−496.68948	−493.72310	−498.54278
PN	−394.99883	−393.08301	−390.59355	−394.61579
HPO	−415.93757	−413.95248	−411.25178	−415.57307
HOCl	−534.70537	−532.24602	−528.93124	−534.24669
NaOH	−237.15607	−235.86888	−234.18866	
NaF	−261.13219	−259.76561	−257.83067	
SiO	−363.62739	−361.84585	−359.40015	
SiH_3F	−389.93313	−388.07406	−385.39137	
ClF	−558.64532	−556.10579	−552.53231	−558.21428
Na_2	−323.68124	−321.70873	−319.39620	
NaCl	−621.38043	−618.24315	−614.52858	
Si_2H_6	−581.19999	−578.24121	−574.70950	
SiH_3Cl	−750.09003	−746.45779	−741.97803	
P_2	−681.34339	−667.97721	−673.76396	−680.60727
P_2H_4	−683.63932	−680.27669	−676.13983	−682.92153
H_2S_2	−796.07652	−792.25614	−787.49104	−795.25760
Cl_2	−918.85350	−914.54394	−909.11517	−917.93916

[a] Nomenclature A//B indicates a calculation of a property at level A performed by using geometry which is optimum for level B. Thus, 3-21G//3-21G indicates a 3-21G level property obtained by using the optimum 3-21G level geometry.

spectively. The lengths of multiple bonds are also given by the theory as consistently too large, although the deviations here are smaller than those for the corresponding single bonds. Both 6-21G and 3-21G basis sets fare reasonably well in calculating the internuclear separation in the weakly bound Na_2 molecule. The STO-3G basis set underestimates the distance by 0.7 Å. The performance of the 6-21G and 3-21G split-valence basis sets, with regard to their overestimation of bond distances, mirrors that of 4-31G; on the other hand, the minimal STO-3G basis set usually yields bond lengths which are shorter than the corresponding experimental values.

Equilibrium bond angles are generally well described at all four basis set levels considered, as are the dihedral angles in P_2H_4 and H_2S_2.

Calculated and experimental equilibrium structures for three hypervalent molecules involving second-row atoms are given in Table VI. Previous experience[8,9] suggests that calculations at the minimal basis set level inadequately describe the bonding in such species, and furthermore that addition of diffuse d-type functions to the basis representation leads to considerable improvement. For example, as the data in the table indicate, at the STO-3G level the calculated equilibrium structure for dimethyl sulfoxide shows an SO bond length of 1.82 Å, to be compared to an experimental value of 1.48 Å. Addition of a set of (five) d-type Gaussian primitives to the representation of the sulfur atom alone (to form the so called STO-3G* basis set[8] for second-row elements) leads to a shortening of this linkage to the point where it is now essentially in perfect accord with the experimental structure. Similar conclusions apply to the remaining molecules in Table VI.

The split-valence 3-21G basis set fares somewhat better than STO-3G in accounting for the geometries of hypervalent molecules, although its performance is also quite poor on an absolute scale. The SO bond length in dimethyl sulfoxide, for example, is shorter than that given at the STO-3G level but is still 0.2 Å away from the experimental value. It is evident that, unsupplemented by diffuse higher-order functions, the 3-21G representation is unsatisfactory for investigations of molecules comprising atoms with expanded valence shells. Efforts to construct small basis sets able to account for the bonding in such species are presently underway.[10]

Molecular Vibration Frequencies. Calculated (6-21G, 3-21G, STO-3G, and 4-31G levels) and experimental fundamental vibration frequencies for hydrogen sulfide and phosphine are compared in Table VII. The theoretical data have been obtained by determination of the complete set of quadratic force constants (second derivatives) evaluated at the calculated equilibrium geometry. Anharmonic effects have been neglected.

As with the previous equilibrium geometry comparisons, results derived from the three split-valence levels show marked similarity, those obtained from the 6-21G and 3-21G calculations being nearly identical. The 6-21G and 3-21G calculations consistently overestimate the magnitudes of frequencies associated largely both with stretching modes (by ~1–4%) and bending modes (by ~10–13%), analogous to the behavior previously reported for compounds containing first-row elements.[2] The performance of the 4-31G basis set with regard to bending frequencies is much the same. On the other hand, 4-31G calculated stretching frequencies for H_2S and PH_3 are lower than the corresponding experimental values. This is opposite the trend noted for compounds of the first row. STO-3G calculated vibration frequencies are in far poorer agreement with the experimental data than are those obtained by using any of the split-valence basis sets. The theoretical values are consistently too large, errors ranging from 25 to 33% for stretching modes and from 36 to 44% for bending modes.

From the limited comparisons presented here, it appears that the new 6-21G and 3-21G levels are at least as successful in reproducing the experimental vibration frequencies of molecules

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(8) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. S. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

(9) A systematic series of investigations on the effect of diffuse d-type functions on the equilibrium geometries of molecules comprising second-row atoms has been carried out by Boggs and co-workers. Split-valence basis sets of similar size to the 3-21G representations presented here have been employed. (a) H. Oberhammer and J. E. Boggs, *J. Mol. Struct.*, **55**, 283 (1979); (b) H. Oberhammer and J. E. Boggs, *ibid.*, **56**, 107, (1979); (c) H. Oberhammer and J. E. Boggs, *ibid.*, **57**, 175 (1979); P. N. Skancke, G. Fogarasi, and J. E. Boggs, *ibid.*, **62**, 259 (1980).

(10) W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople, and J. S. Binkley, *J. Am. Chem. Soc.*, in press.

Table IX. Calculated and Experimental Energies of Hydrogenation Reactions (kcal mol^{-1})

hydrogenation reaction	6-21G// 6-21G[a]	3-21G// 3-21G[a]	STO-3G// STO-3G[a]	4-31G// 4-31G[a]	exptl[b]
$Li\text{-}Cl + H_2 \rightarrow LiH + HCl$	68.6	71.7	69.3	70.9	60
$CH_3\text{-}SiH_3 + H_2 \rightarrow CH_4 + SiH_4$	−12.7	−11.2	−9.8		−8
$CH_3\text{-}SH + H_2 \rightarrow CH_4 + H_2S$	−20.8	−20.3	−17.2	−21.3	−16
$CH_3\text{-}Cl + H_2 \rightarrow CH_4 + HCl$	−21.6	−21.3	−14.0	−21.1	−21
$Na\text{-}OH + H_2 \rightarrow NaH + H_2O$	14.0	15.5	15.4		21
$HOCl + H_2 \rightarrow H_2O + HCl$	−53.6	−54.2	−33.4	−62.1	−61
$Na\text{-}F + H_2 \rightarrow NaH + HF$	27.9	29.6	37.4		34
$SiH_3\text{-}F + H_2 \rightarrow SiH_4 + HF$	29.5	31.3	11.8		46
$Cl\text{-}F + H_2 \rightarrow HCl + HF$	−62.4	−63.3	−37.1	−68.7	−78
$Na\text{-}Na + H_2 \rightarrow 2NaH$	42.4	43.5	73.9		30
$NaCl + H_2 \rightarrow NaH + HCl$	68.9	72.5	122.0		52
$SiH_3\text{-}SiH_3 + H_2 \rightarrow 2SiH_4$	−8.1	−8.1	−5.0		−3
$SiH_3\text{-}Cl + H_2 \rightarrow SiH_4 + HCl$	13.2	15.3	22.9		33
$PH_2\text{-}PH_2 + H_2 \rightarrow 2PH_3$	−9.4	−7.8	−9.7	−7.6	−5
$Cl\text{-}Cl + H_2 \rightarrow 2HCl$	−46.5	−45.2	−24.7	−38.2	−45

[a] See footnote *a* of Table VII. [b] Experimental reaction energies based on heats of formation given in ref 10 and corrected for zero-point vibrations.

containing second-row elements as they were for compounds of the first row. In addition, the results at the smaller of these levels (3-21G) are comparable to those obtained by using the more costly 4-31G representation and far superior to those derived from the minimal STO-3G basis set.

Hydrogenation Energies. 6-21G and 3-21G total energies for all molecules previously discussed (except for hypervalent species) are presented in Table VIII, along with previously obtained STO-3G and 4-31G values (some of which have already appeared in the literature).[3c,4b,8] Experimental gas-phase heats of formation and zero-point vibrational energies may be found in ref 10. We shall not consider these data as such; rather they will be employed in order to assess the performance of the theory in the calculation of energy differences.

Only limited gas-phase experimental thermochemical data are available for molecules containing second-row elements, most of which are restricted to very simple (one- and two-heavy-atom) systems. In practice, therefore, comprehensive comparisons of calculated and experimental reaction energies are possible only for a few very elementary processes involving simple molecules. The most notable of these is perhaps the general hydrogenation reaction in which a molecule comprising two or more heavy atoms is reduced to a set of one-heavy-atom hydrides. The comparison is presented in Table IX. The performance of three split-valence basis sets with regard to the calculation of hydrogenation energies is markedly similar. The largest discrepancy between the 6-21G and 3-21G levels is 3.6 kcal mol^{-1}; that between 3-21G and 4-31G is 8.3 kcal mol^{-1}. Deviations from experiment are sometimes significantly greater, approximately 10 and 20 kcal mol^{-1} for the hydrogenation of LiCl and NaCl, respectively. In general, the STO-3G minimal basis set fares worse, especially in reactions involving either very electropositive elements (e.g., sodium) or very electronegative ones (e.g., chlorine).

Electric Dipole Moments. Theoretical and experimental electric dipole moments for a number of one- and two-heavy-atom molecules containing second-row elements are compared in Table X.

Table X. Calculated and Experimental Electric Dipole Moments (D)

molecule	6-21G// 6-21G[a]	3-21G// 3-21G[a]	STO-3G// STO-3G[a]	4-31G// 4-31G[a]	exptl
NaH	6.90	7.01	5.72		6.96
PH_3	1.26	1.24	0.65	1.07	0.58
H_2S	1.85	1.83	1.03	1.78	0.97
HCl	1.87	1.86	1.76	1.87	1.08
LiCl	8.07	8.13	5.41	7.68	7.13
CH_3SiH_3	0.63	0.63	0.07		0.74
HCP	0.90	0.87	0.04	0.511	0.39
CH_3PH_2	1.41	1.39	0.53	1.02	1.10
CS	0.77	0.85	1.01	0.89	1.98
CH_3SH	2.14	2.12	0.96	1.98	1.52
CH_3Cl	2.86	2.86	2.33	2.74	1.87
NaF	7.50	7.54	6.20		8.16
SiH_3F	1.87	1.87	1.02		1.27
ClF	1.21	1.13	0.57	1.69	0.88
NaCl	10.12	10.16	9.14		9.00
SiH_3Cl	3.48	3.53	3.06		1.31

[a] See footnote *a* of Table VII. [b] Experimental dipole moments from R. D. Nelson, D. R. Lide, and A. A. Maryott, *Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 10 (1967).

Values derived from the three split-valence levels are generally similar to each other, and in most instances are larger than the corresponding experimental quantities. Calculated STO-3G electric dipole moments are consistently smaller than those obtained at the higher levels of theory and, with few exceptions, underestimate the experimental values. These same trends have already been noted for simple molecules containing first-row elements. None of the theoretical methods considered here fare very well either in obtaining absolute values of electric dipole moments or in quantitatively ascertaining substituent effects on dipole moment magnitudes. It would appear that higher-level theoretical treatments are required.