

A Systematic Preparation of New Contracted Gaussian-Type Orbital Sets. VI. *Ab Initio* Calculation on Molecules Containing Na Through Cl

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Compact contracted Gaussian basis sets introduced in the preceding article are tested for *ab initio* molecular calculations on molecules containing third-row atoms (Na through Cl). It is found that the effect of splitting valence orbitals is essential for these molecules and addition of polarization functions to split basis sets can yield computed geometries, spectroscopic constants, and atomization energies in close agreement with the result of near Hartree–Fock calculations.

I. INTRODUCTION

A number of *ab initio* molecular calculations are carried out for molecules containing the third-row atoms (Na through Cl) using various contracted Gaussian basis sets that were newly developed in a systematic way.^{1,2} Only closed-shell ground-state electron configurations are treated. The method of calculation is the restricted Roothaan–Hartree–Fock SCF method and all the calculations are performed by a modified version³ of MOLECULE originally developed by Almlöf.⁴

The basis sets tested are minimal basis sets MINI-*i*, and split basis sets MIDI-*i* and SMIDI-*i* (*i* = 1, 3, and 4), which were introduced in the preceding article. 3GTO given by Duijneveldt⁵ is used throughout this article as the basis set of the hydrogen atom.

The basis sets for the second-row atoms (O and F) are taken from a previous article.¹ In addition to these basis sets, MINI-*i** and MIDI-*i**, in which one polarization function is added to MINI-*i* and MIDI-*i*, respectively, are also tested.

Total energies, atomization energies, equilibri-

um geometries, and spectroscopic constants are calculated. They are compared with the experimental values and the values given by the accurate calculations. It is found that the effect of splitting valence orbitals is substantial for the molecules considered in the present work. The error of bond lengths by MIDI-*i* is reduced to about one-half of those by MINI-*i* for almost all molecules tested here. The MIDI-*i* also give satisfactory values for orbital energies and spectroscopic constants. Addition of polarization functions brings further improvements: the MIDI-*i** sets give geometries, spectroscopic constants, and atomization energies, which agree fairly well with those given by the accurate calculations.

Pople's group has also performed a number of calculations on molecules containing third-row atoms with STO-3G, 44-31G, and STO-3G*.⁶ In STO-3G* sets, *d*-type polarization functions are added to the STO-3G basis for the third-row atoms only. MINI-1 is to be compared with STO-3G.⁷ Both basis sets have the same number of primitive GTOs. 44-31G sets have been published only for P, S, and Cl.⁸ The size of these basis sets is (4431/431) in our notation and it is larger than all of our MIDI-*i* (*i* = 1, 3, and 4). In the STO-3G and the 44-31G basis sets, the same orbital exponents are

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Table I. Optimum scale factors for H₂S, SO₂, HCl, and Cl₂.^a

Molecule	Atom	Function	MINI-1	MINI-3 ^b	MINI-4 ^c
H ₂ S	S	3s	1.012	1.007	(1.007)
		3p	1.028	1.028	(1.028)
SO ₂	O	2s	0.995	0.989	(0.989)
		2p	0.970	(0.970)	(0.970)
	S	3s	1.042	1.037	(1.037)
		3p	1.130	(1.130)	(1.130)
HCl	Cl	3s	1.005	1.001	1.001
		3p	1.010	1.010	1.004
Cl ₂	Cl	3s	1.005	1.002	1.003
		3p	1.015	1.015	1.010

^a Scale factor for H is always fixed to 1.188, which has been previously determined for H₂ (see ref. 1).

^b Values enclosed in parentheses are fixed to the corresponding values of MINI-1.

^c Values enclosed in parentheses are fixed to the corresponding values of MINI-3.

used for both *s*-type and *p*-type functions, e.g., $\zeta_{2s} = \zeta_{2p}$ and $\zeta_{3s} = \zeta_{3p}$, and the exponents have been rescaled for the basis sets used for molecular calculations. It was found that neither STO-3G nor 44-31G gives a reliable prediction of bond lengths. STO-3G* gives only marginally better bond lengths than STO-3G and 44-31G. The MIDI-*i* basis sets give a more reliable prediction of bond lengths than STO-3G*, and MIDI-*i** consistently gives very good agreement with experimental bond lengths.

II. PILOT CALCULATIONS

Pilot calculations have been performed for HCl, Cl₂, SO₂, and SH₂ with all kinds of basis sets mentioned in the Introduction. The exponents of the valence shell orbitals in the MINI-*i* basis sets were scaled for individual molecules, while the scale factor for the hydrogen atom in MINI-*i* basis sets was always fixed to 1.188, which was determined previously for H₂.¹ The resulting scale factors are given in Table I. It is seen in this table that the values of scale factors are around 1.0 in almost all cases. However, the value for the 3*p* orbital of S in SO₂ (1.130) is rather large and considerably different from the corresponding value (1.028) for S in H₂S.

A single standard scale factor for each atom may be established by averaging over values obtained from a chosen set of molecular calculations, as Pople's group did for the STO-3G and 4-31G basis sets. However, the gain in overall performance is only of a statistical nature without convincing physical justification, because the averaging does not reflect peculiarities in molecular environments such as electronegativity differences in various combinations of atoms in molecules. Furthermore, it introduces semiempiricism into the alleged *ab initio* molecular calculation. Based on these considerations we have decided that all scale factors be fixed to 1.0 for MINI-*i* basis sets, except for H which is assigned the value 1.188. Furthermore, no scale factor has been used for the split orbitals, SMIDI-*i*, MIDI-*i*, and MIDI-*i**, even for H. Instead, we expected that the flexibility of the basis sets introduced by splitting the valence orbitals would accommodate various molecular environments.

The exponents of the polarization functions have been determined in the same way as done in the previous work,¹ in which the radial overlap integral between the polarization function and the valence orbital was maximized. As the polarization functions, *d*-type GTOs are taken for Al through Ar, while *p*-type GTOs are used for Na and Mg. The exponents of the polarization functions are given in Table II. The polarization functions for H, O, and F have been taken from ref. 1.

Total energies (t.e.), atomization energies (a.e.), and computed geometries are given in Tables III–VI and compared with those of experimental, extended calculation, STO-3G, 44-31G, and STO-

Table II. Exponents of polarization functions.

Atom	p.f. ^a	Exponent	Atom	p.f. ^a	Exponent
Na	2p	0.06	P	3d	0.37
Mg	2p	0.16	S	3d	0.46
Al	3d	0.21	Cl	3d	0.56
Si	3d	0.28	Ar	3d	0.68

^a p.f. is polarization function.

Table III. Total energy, atomization energy, geometry, and spectroscopic constants of HCl ($^1\Sigma^+$).^a

Basis sets ^{b,c}	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G	-455.13601	3.46	1.313			
44-31G	-459.56342	2.55	1.299			
STO-3G*	-455.15788	3.95	1.287			
(MINI-1)/MINI-1	-457.84352	2.41	1.363	3050	9.260	0.538E+06
(MINI-1)/MINI-1)	-457.84376	2.42	1.358	3040	9.320	0.533E+06
(MINI-1)/MINI-3)	-459.11866	2.39	1.358	3110	9.330	0.558E+06
(MINI-1)/MINI-4)	-459.52799	2.31	1.363	3060	9.260	0.540E+06
MIDI-1/SMIDI-3	-459.18532	2.52	1.308	2900	10.100	0.485E+06
(MINI-1)/MIDI-1	-457.92108	2.45	1.319	2850	9.880	0.470E+06
(MINI-1)/MIDI-3	-459.18670	2.44	1.319	2850	9.880	0.470E+06
(MINI-1)/MIDI-4	-459.54534	2.45	1.318	2850	9.900	0.470E+06
MIDI-1/MIDI-1	-457.92590	2.58	1.297	2920	10.200	0.492E+06
MIDI-1/MIDI-3	-459.19103	2.56	1.298	2920	10.200	0.491E+06
MIDI-1/MIDI-4	-459.54966	2.56	1.297	2920	10.200	0.491E+06
MIDI-1/MIDI-3*	-459.22088	3.13	1.284	3120	10.400	0.561E+06
(MINI-1*)/MINI-1*)	-457.92457	3.34	1.311	3260	10.000	0.614E+06
(MINI-1*)/MINI-3*)	-459.16364	3.29	1.311	3260	10.000	0.613E+06
(MINI-1*)/MINI-4*)	-459.57081	3.15	1.314	3210	9.960	0.594E+06
(MINI-1*)/MIDI-1*	-457.98945	3.33	1.284	3190	10.400	0.588E+06
(MINI-1*)/MIDI-3*	-459.22755	3.31	1.284	3190	10.400	0.588E+06
(MINI-1*)/MIDI-4*	-459.58610	3.32	1.283	3180	10.500	0.585E+06
MIDI-1*/MIDI-1*	-457.99114	3.37	1.278	3160	10.500	0.578E+06
MIDI-1*/MIDI-3*	-459.22887	3.35	1.278	3160	10.500	0.576E+06
MIDI-1*/MIDI-4*	-459.58739	3.35	1.277	3160	10.500	0.575E+06
Extended ^d	-460.1104	3.48	1.264	3181	10.77	0.584E+06
Exptl. ^e		4.61	1.275	2990	10.59	0.516E+06

^a The data of STO-3G, 44-31G, and STO-3G* are taken from ref. 6.

^b Basis sets enclosed in parentheses denote the scaled basis sets with the scale factors given in Table I.

^c Basis set on the left-hand side is used for the light atom (H, O, and F) in a molecule and that on the right-hand side is used for the heavy atom (Na through Cl); e.g., MIDI-1/SMIDI-3 indicates that MIDI-1 is used for H and SMIDI-3 is used for Cl in HCl.

^d P. E. Cade and W. M. Huo, *J. Chem. Phys.*, **47**, 649 (1967).

^e Experimental values are taken from *JANAF Thermochemical Tables*, 2nd ed., D. R. Stull and H. Prophet, Eds., U.S. Department of Commerce, Washington, DC, 1971. Atomization energy has been calculated from the experimental data by taking the zero-point energy into account.

3G*. Spectroscopic constants (vibrational constants ω_e , rotational constants B_e , and force constants κ_e) have also been calculated for diatomic molecules with third-degree polynomial fitting.⁹ The results are included in Tables III and IV.

The results calculated with the nonscaled MINI-1 sets are given just above the data for the scaled MINI-1 sets. It is seen that the nonscaled MINI-1 sets give comparable results with the scaled MINI-1 sets.

It is to be noted in Tables III–VI that three kinds of basis sets of the same group (e.g., MINI-1, MINI-3, and MINI-4 in the MINI-*i* group) give essentially the same geometries and spectroscopic constants, while they give different values for atomization energies.

In other words, if we are interested in molecular geometries and spectroscopic constants, it is not cost effective to use many primitive Gaussian functions for the inner-core orbitals, while splitting

Table IV. Total energy, atomization energy, geometry, and spectroscopic constants of Cl_2 ($^1\Sigma_g^+$).^a

Basis sets	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm^{-1})	B_e (cm^{-1})	κ_e (dyn/cm)
STO-3G	-909.11517	0.837	2.063			
44-31G	-917.93916	-0.104	2.177			
STO-3G*	-909.16444	1.956	1.967			
MINI-1	-914.51574	-0.001	2.184	579	0.199	0.350E+06
(MINI-1)	-914.51791	0.058	2.167	596	0.202	0.371E+06
(MINI-3)	-917.06888	0.032	2.172	582	0.201	0.353E+06
(MINI-4)	-917.88725	-0.134	2.185	578	0.199	0.348E+06
SMIDI-3	-917.18689	-0.130	2.190	553	0.198	0.319E+06
MIDI-1	-914.66386	-0.118	2.188	538	0.199	0.302E+06
MIDI-3	-917.19488	-0.135	2.188	537	0.199	0.302E+06
MIDI-4	-917.91127	-0.152	2.187	539	0.199	0.303E+06
(MINI-1*)	-914.65171	1.150	2.044	635	0.228	0.422E+06
(MINI-3*)	-917.12960	1.050	2.045	625	0.227	0.408E+06
(MINI-4*)	-917.94464	0.784	2.061	621	0.224	0.403E+06
MIDI-1*	-914.77286	0.881	2.021	594	0.233	0.368E+06
MIDI-3*	-917.24888	0.851	2.020	596	0.233	0.371E+06
MIDI-4*	-917.96527	0.837	2.019	588	0.233	0.361E+06
Extended ^b	-918.99012	1.16	2.000	564	0.238	0.332E+06
Exptl. ^c		2.51	1.986	561	0.241	0.329E+06

^a See footnotes a and b to Table III.^b P. A. Straub and A. D. McLean, *Theor. Chim. Acta*, **32**, 227 (1974). R_e and spectroscopic constants have been recalculated in O. Gropen, S. Huzinaga, and A. D. McLean, *J. Chem. Phys.*, **73**, 402 (1980).^c See footnote e to Table III.

the valence orbitals and adding the polarization functions are very effective means for making good computational predictions of these molecular properties. However, the "hardness" of the inner part of the basis sets works to decrease total energies and to get reliable atomization energies. As shown in Tables III–VI, the quality of the computed data is improved markedly by going from MINI- i to MIDI- i with the only exception being Cl_2 .

The effectiveness of both split valence orbitals and polarization functions is very much evident in the MIDI- i^* sets and they give geometries and spectroscopic constants which agree fairly well with those given by extended calculations. The MINI- i^* sets, in which the same scale factors as MINI- i are used, give better values than MINI- i and MIDI- i sets but they are not quite as good as those of MIDI- i^* . As for the atomization energies, the values seem to converge in going from MIDI-3* to MIDI-4* and they are close to the values given

by extended calculation, while the values do not converge in going from MINI-3* to MINI-4*.

The SMIDI-3/MIDI-3* sets (SMIDI-3 is used for H or second-row atoms and MIDI-3* is used for third-row atoms) have also been tested and it has been found that the results are always superior to MINI- i^* , while the computational time for SMIDI-3/MIDI-3* is much shorter than that for MINI- i^* . Therefore, we have decided not to continue calculations with MINI- i^* . Calculations with SMIDI- i , MIDI- i , and MIDI- i^* basis sets have been extended to 11 other molecules. Calculations with nonscaled MINI-1 basis sets have also been extended to those molecules where only the exponent of hydrogen is always scaled. From the results of the pilot calculations, 3GTO basis set⁵ seems to be enough for the hydrogen atom. Therefore, throughout the present work, 3GTO basis set has been used for hydrogen, (3) is named as MINI-1 and (21) is named as MIDI-1. The results are summarized in Tables VII–XVII.

Table V. Total energy, atomization energy, and geometry of SO₂ (¹A₁).^a

Basis sets ^b	t.e. (a.u.)	a.e. (eV)	R _e (Å)	θ (deg)
STO-3G	-540.64868	-2.45	1.562	109.2
44-31G	-546.37328	-2.34	1.531	115.1
STO-3G*	-540.91012	4.54	1.446	119.9
MINI-1	-544.03184	-4.93	1.659	108.6
(MINI-1)	-544.07847	-3.66	1.600	110.0
(MINI-3)	-545.78456	-3.87	1.606	109.5
(MINI-4)	-546.25500	-4.56	1.620	109.8
SMIDI-3	-545.86419	-3.13	1.575	112.8
SMIDI-3/MIDI-3	-545.89818	-2.30	1.538	112.4
MIDI-1	-544.25957	-1.89	1.523	115.9
MIDI-3	-545.92171	-2.01	1.516	115.6
MIDI-4	-546.36440	-2.27	1.527	114.1
SMIDI-3/MIDI-3*	-546.05542	1.77	1.454	118.7
(MINI-1*)	-544.36210	2.50	1.458	117.5
(MINI-3*)	-546.00788	1.91	1.463	117.4
(MINI-4*)	-546.48471	1.39	(1.463) ^f	(117.4) ^e
MIDI-1*	-544.49831	3.19	1.437	118.1
MIDI-3*	-546.11849	3.11	1.438	118.1
MIDI-4*	-546.57233	3.15	(1.438) ^e	(118.1) ^e
Extended ^c	-547.22464	3.81	1.423	118.4
Exptl. ^d		11.22	1.432	119.5

^a See footnote a to Table III.^b See footnotes b and c to Table III.^c Reference 11.^d See footnote e to Table III.^e No geometry optimization has been done for MINI-4* and MIDI-4*, t.e. and a.e. were calculated at the fixed geometry.

III. RESULTS AND DISCUSSION

Fifteen molecules are the subject of the present investigation, including four molecules chosen for pilot calculations, and the results of calculations and the pertinent discussions are presented in the following.

A. Geometries

As mentioned in the previous section, three orbitals of the same type (e.g., MINI-1, MINI-3, and MINI-4 in the MINI group) give essentially the same values for geometries and spectroscopic constants. Therefore, for the sake of brevity, we picked up the values of $i = 1$ from the original Tables III–XVII and summarized R_e and θ_e in

Table XVIII. For SMIDI- i and SMIDI- i /MIDI- i * sets, only the $i = 3$ case has been calculated, so that the values for $i = 3$ are shown in this table. In Table XVIII, if the molecules contain H, Na, and Mg, for which no SMIDI-3 is defined, the values calculated with MIDI-3 for those atoms are given as the values for SMIDI-3, and if the molecules do not contain any second-row atoms, the data by MIDI-3* are given as those for SMIDI-3/MIDI-3*. In Table XVIII the values for STO-3G, 44-31G, and STO-3G* are also shown, and those values are compared with the experimental data as well as those of our basis sets. Numbers in parentheses indicate the error defined as follows:

$$\text{Error} = [(R_e^{\text{cal}} - R_e^{\text{expt}})/R_e^{\text{expt}}] \times 100 (\%) \quad (1)$$

Table VI. Total energy, atomization energy, and geometry of H₂S (¹A₁).^a

Basis sets ^b	t.e. (a.u.)	a.e. (eV)	R _e (Å)	θ (deg)
STO-3G	-394.31163	6.76	1.329	92.5
44-31G	-398.20395	4.30	1.354	95.6
STO-3G*	-394.34444	7.52	1.318	91.8
(MINI-1)/MINI-1	-396.67554	4.00	1.413	94.7
(MINI-1)/(MINI-1)	-396.67804	4.07	1.396	94.3
(MINI-1)/(MINI-3)	-397.80939	4.01	1.400	94.3
MIDI-1/SMIDI-3	-397.87048	4.25	1.355	95.8
(MINI-1)/MIDI-1	-396.74449	4.15	1.357	95.5
(MINI-1)/MIDI-3	-397.86974	4.14	1.358	95.9
MIDI-1/MIDI-1	-396.75043	4.31	1.351	95.8
MIDI-1/MIDI-3	-397.87506	4.28	1.352	95.8
MIDI-1/SMIDI-3*	-397.91966	5.29	1.345	93.8
(MINI-1*)/(MINI-1*)	-396.77291	5.60	1.364	92.9
(MINI-1*)/(MINI-3*)	-397.87496	5.52	1.363	92.8
(MINI-1*)/MIDI-1*	-396.82611	5.53	1.342	93.8
(MINI-1*)/MIDI-3*	-397.92811	5.52	1.342	93.7
MIDI-1*/MIDI-1*	-396.82793	5.58	1.343	93.8
MIDI-1*/MIDI-3*	-397.92925	5.55	1.342	93.8
Extended	-398.6862 ^c	5.58 ^c	1.329 ^d	94.1 ^d
Exptl.		6.96 ^c	1.328 ^e	92.2 ^e

^a See footnote a to Table III.^b See footnotes b and c to Table III.^c S. Rothenberg, R. H. Young, and H. F. Schaefer III, *J. Am. Chem. Soc.*, **92**, 3243 (1970).^d M. F. Guest and W. R. Rodwell, *Mol. Phys.*, **32**, 1075 (1976).^e See footnote e to Table III.

where R_e^{cal} and R_e^{expt} are calculated and experimental equilibrium internuclear distances, respectively. In Fig. 1, the errors for MINI-1, MIDI-1, and SMIDI-3/MIDI-3* are plotted and those for STO-3G, 44-31G, and STO-3G* are also plotted in Fig. 2. For MINI-1, the values obtained with nonscaled MINI-1 are shown in both Table XVIII and Fig. 1; scaled MINI-1 sets give slightly better results than nonscaled MINI-1 sets. For MgH₂, no experimental value is available so that the values of extended calculation are given instead. The data for Na₂ and Si₂ are omitted from Figs. 1 and 2 because errors for STO-3G and STO-3G* are much too large to be included in Fig. 2.

Let us discuss R_e in Fig. 1. It is clearly seen that the error is reduced markedly from MINI-1 to

MIDI-1 and from MIDI-1 to SMIDI-3/MIDI-3*. Mean values of |Error| over all 15 molecules are 6.8, 3.5, and 1.8% for MINI-1, MIDI-1, and SMIDI-3/MIDI-3*, respectively. If Na₂ and Si₂ are excluded, the corresponding values are 7.3, 3.4, and 1.1%. It should be noted that computed R_e with the MINI-1 set is always longer than the experimental R_e , except for NaH and MgH₂. Generally speaking, splitting valence orbitals makes bond lengths shorter and addition of polarization functions works in the same direction, so that computed bond lengths become closer to the experimental ones. The values of NaH and MgH₂ for MINI-1 are rather curious. This might be because the scale factor for the 1s orbital of hydrogen has been taken to be 1.188 and so that 1s orbital is

Table VII. Total energy, atomization energy, geometry, and spectroscopic constants of NaCl ($^1\Sigma_g$).^a

Basis sets	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G	-614.52858	8.65	2.221			
STO-3G*	-614.59684	10.40	2.175			
MINI-1	-618.19783	1.73	2.403	354	0.209	0.103E+06
SMIDI-3	-620.10845	2.44	2.391	367	0.211	0.111E+06
MIDI-1	-618.30510	2.56	2.386	371	0.212	0.113E+06
MIDI-3	-620.11598	2.54	2.386	375	0.212	0.115E+06
MIDI-4	-620.67243	2.46	2.404	365	0.209	0.109E+06
MIDI-1*	-618.36878	2.96	2.352	380	0.219	0.119E+06
MIDI-3*	-620.15185	2.92	2.356	381	0.218	0.119E+06
MIDI-3*	-620.70103	2.90	2.365	376	0.216	0.116E+06
Extended ^b	-621.45743	3.19	2.374	377	0.214	0.117E+06
Exptl. ^c		4.24	2.361	364	0.217	0.109E+06

^a See footnote a to Table III.^b The values have been calculated with third-degree polynomial fitting by using the total energy data given by A. D. McLean and M. Yoshimine, *Table of Linear Molecule Wavefunctions*, IBM, San Jose, 1967.^c See footnote e to Table III.

more contracted than in a neutral hydrogen atom. We have good reason to be curious about the deviant results of MINI-1 calculations for NaH and MgH₂. We suspect that it may be because the hydrogen atom in these molecules might be nega-

tively rather than positively charged. This is one of the reasons why we have decided to abandon the idea of the scale factor altogether for MIDI-*i*, SMIDI-*i*, and MIDI-*i** sets. The SMIDI-*i*/MIDI-*i** set always gives excellent agreement with

Table VIII. Total energy, atomization energy, geometry, and spectroscopic constants of P₂ ($^1\Sigma_g^+$).^a

Basis sets	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G	-673.76396	0.720	1.808			
44-31G	-680.60727	-0.763	1.949			
STO-3G*	-673.86766	3.543	1.756			
MINI-1	-677.92441	-1.23	2.020	800.	0.267	0.583E+06
SMIDI-3	-680.02150	-1.07	1.980	795.	0.278	0.577E+06
MIDI-1	-678.05723	-0.613	1.928	832.	0.293	0.631E+06
MIDI-3	-680.04225	-0.636	1.930	830.	0.292	0.629E+06
MIDI-4	-680.60991	-0.645	1.927	832.	0.293	0.631E+06
MINI-1*	-678.07479	1.16	1.901	909.	0.301	0.754E+06
MIDI-1*	-678.18356	1.40	1.871	917.	0.311	0.767E+06
MIDI-3*	-680.12828	1.35	1.871	915.	0.311	0.764E+06
MIDI-4*	-680.69555	1.34	1.869	914.	0.311	0.761E+06
Extended ^b	-681.50039	---	1.851	920	0.318	0.772E+06
Exptl. ^c		5.08	1.894	780	0.303	0.555E+06

^a See footnote a to Table III.^b R. S. Mulliken and B. Liu, *J. Am. Chem. Soc.*, **93**, 6738 (1971).^c See footnote c to Table III.

Table IX. Total energy, atomization energy, geometry, and spectroscopic constants of NaH ($^1\Sigma^+$).^a

Basis sets ^b	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G	-160.31570	4.917	1.654			
STO-3G*	-160.33999	5.567	1.725			
(MINI-1)/MINI-1	-161.35789	-0.423	1.776	1400	5.54	0.111E+06
(MINI-1)/(MINI-1) ^c	-161.36007	-0.364	1.760	1480	5.64	0.124E+06
MIDI-1/MIDI-1	-161.40008	0.710	1.875	1240	4.85	0.897E+05
MIDI-1/MIDI-3	-161.94588	0.709	1.875	1260	4.96	0.901E+05
MIDI-1/MIDI-3*	-161.96190	0.796	1.926	1140	4.70	0.740E+05
MIDI-1*/MIDI-1*	-161.41793	0.851	1.892	1190	4.88	0.809E+05
MIDI-1*/MIDI-3*	-161.96383	0.848	1.893	1210	4.87	0.827E+05
Extended ^d	-162.3929	0.932	1.914	1187	4.77	0.802E+05
Exptl. ^e		2.12	1.887	1172	4.90	0.781E+05

^a See footnote a to Table III.^b See footnotes b and c to Table III.^c Optimized scale factor for 3s of Na (1.083) was used for this calculation, where the scale factor for H was taken to be 1.188.^d See footnote d to Table III.^e See footnote e to Table III.

experimental values and the values given by extended calculation and so does the MIDI-*i** set.

Now we shall assess the overall performance of STO-3G, STO-3G*, and 44-31G proposed by Pople's group. In these basis sets, the same orbital exponents are used for both *s*-type and *p*-type

functions, e.g., $\zeta_{2s} = \zeta_{2p}$ and $\zeta_{3s} = \zeta_{3p}$, and the exponents have been rescaled for the basis sets used for molecular calculations. In STO-3G*, *d*-type polarization functions are added only to the basis sets of the third-row atoms.

Figure 2 is a graphic summary of errors defined

Table X. Total energy, atomization energy, geometry, and spectroscopic constants of AlF ($^1\Sigma^+$).^a

Basis sets ^b	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G	-337.04264	5.38	1.616			
STO-3G*	-337.12600	7.51	1.563			
MINI-1	-339.44348	3.08	1.666	826	0.545	0.449E+06
SMIDI-3	-340.63253	3.96	1.672	825	0.541	0.447E+06
MIDI-1	-339.56257	4.36	1.664	878	0.546	0.507E+06
MIDI-3	-340.65507	4.31	1.665	875	0.546	0.503E+06
SMIDI-3/MIDI-3*	-340.68368	5.20	1.653	933	0.553	0.571E+06
MINI-1*	-339.54667	5.08	1.618	978	0.578	0.628E+06
MIDI-1*	-339.62840	5.34	1.638	941	0.563	0.581E+06
MIDI-3*	-340.69668	5.31	1.639	938	0.563	0.578E+06
Extended ^c	-341.48326	5.38	1.653	856	0.553	0.481E+06
Exptl. ^d		6.95	1.655	802	0.552	0.422E+06

^a See footnote a to Table III.^b See footnote c to Table III.^c See footnote b to Table VII.^d See footnote e to Table III.

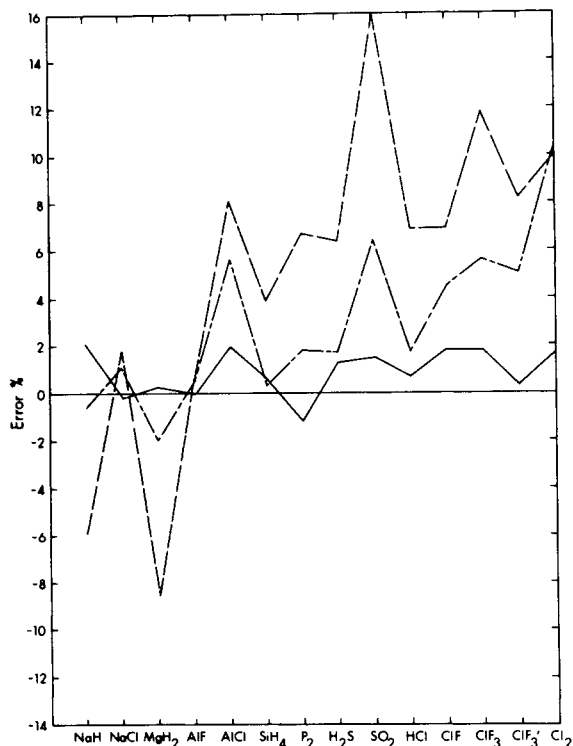


Figure 1. Error of calculated bond lengths (R_e) for (---) MINI-1, (- - -) MIDI-1, and (—) SMIDI-3/MIDI-3*.

in eq. (1) by using Pople's STO-3G, 44-31G, and STO-3G*. Figure 2 is to be compared with Fig. 1 where errors from our basis sets, MINI-1, MIDI-1, and SMIDI-3/MIDI-3*, are shown graphically. The STO-3G errors in Fig. 2 are to be compared

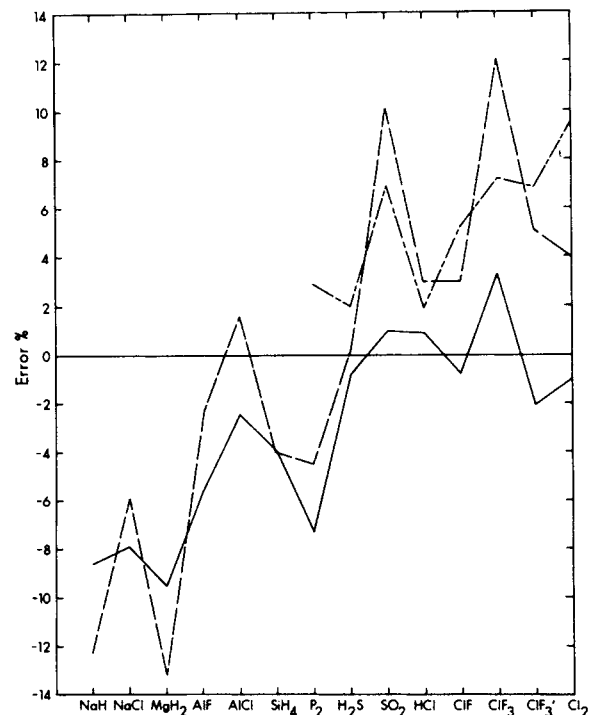


Figure 2. Error of calculated bond lengths (R_e) for (---) STO-3G, (- - -) 44-31G, and (—) STO-3G*.

with those of MINI-1 in Fig. 1. Both basis sets are comparable in overall performance but some of the STO-3G results are notably erratic. Figure 2 shows that the STO-3G errors have negative sign for about half of the molecules treated here. In this circumstance, addition of polarization functions

Table XI. Total energy, atomization energy, geometry, and spectroscopic constants of AlCl ($^1\Sigma^+$).^a

Basis sets	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G	-693.65695	6.98	2.164			
STO-3G*	-693.69651	7.80	2.078			
MINI-1	-697.92520	3.09	2.303	433	0.207	0.169E+06
SMIDI-3	-700.06004	3.30	2.290	413	0.210	0.154E+06
MIDI-1	-698.05300	3.50	2.252	421	0.217	0.160E+06
MIDI-3	-700.07166	3.47	2.258	448	0.216	0.181E+06
MIDI-1*	-698.13058	4.20	2.171	472	0.233	0.201E+06
MIDI-3*	-700.10978	4.15	2.173	470	0.233	0.199E+06
Extended Exptl. ^b		5.16	2.130	480	0.243	0.208E+06

^a See footnote a to Table III.

^b See footnote e to Table III.

Table XII. Total energy, atomization energy, geometry, and spectroscopic constants of FCl ($^1\Sigma^+$).^a

Basis sets	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G	-552.53231	0.100	1.677			
44-31G	-558.21428	-0.616	1.714			
STO-3G*	-552.58869	1.522	1.615			
MINI-1	-556.01174	-0.617	1.741	892	0.450	0.579E+06
SMIDI-3	-557.72079	-0.521	1.721	855	0.460	0.533E+06
MIDI-1	-556.12952	-0.449	1.702	845	0.471	0.520E+06
MIDI-3	-557.73487	-0.479	1.704	843	0.469	0.518E+06
SMIDI-3/MIDI-3* ^b	-557.75800	0.138	1.658	888	0.496	0.575E+06
MIDI-1*	-556.21225	0.431	1.627	921	0.515	0.618E+06
MIDI-3*	-557.77682	0.411	1.629	917	0.513	0.612E+06
Extended ^c	-558.90277	0.757	1.585	912	0.542	0.606E+06
Exptl.		2.665	1.628	784	0.514	0.448E+06

^a See footnote a to Table III.^b See footnote c to Table III.^c See footnote b to Table IV.^d See footnote e to Table III.

would not result in a consistent improvement of computed bond lengths because the addition usually shortens the bond length. This expectation can be graphically confirmed in Fig. 2.

Especially troublesome are NaH, MgH₂, Na₂, and Si₂. Na₂ and Si₂ are excluded from Fig. 2 (and

accordingly also from Fig. 1) because errors for them are too large; these are given numerically in Table XVIII. As noted in the preceding section, the main source of these large errors may be traced to the use of the standard molecular exponents in Pople's basis sets.

Table XIII. Total energy, atomization energy, geometry, and spectroscopic constants of Na₂ ($^1\Sigma_g^+$).

Basis sets	t.e. (a.u.)	a.e. (eV)	R_e (Å)	ω_e (cm ⁻¹)	B_e (cm ⁻¹)	κ_e (dyn/cm)
STO-3G ^a	-318.59246	-20.3	2.259	535	0.287	0.194E+06
STO-3G* ^a	-319.30367	-0.903	2.652	254	0.208	0.438E+05
MINI-1	-321.74771	-0.142	3.230	152	0.141	0.156E+05
MIDI-1	-321.74886	-0.140	3.199	144	0.143	0.140E+05
MIDI-2	-322.84053	-0.140	3.194	150	0.144	0.152E+05
MIDI-1*	-321.78019	0.022	3.235	155	0.140	0.164E+05
MIDI-2*	-322.87216	0.022	3.227	159	0.141	0.171E+05
Extended		0.022 ^c	---	---	---	---
Exptl. ^b		0.797	3.079	159	0.155	0.171E+05

^a Since no data are available in ref. 6, we have performed the calculation for this molecule by using STO-3G and STO-3G* given by Pople's group. Atomization energy has been calculated in the same way as in ref. 6. See Sec. III C for details.

^b See footnote e to Table III.

^c From Table 2 of Martin and Davidson, *Mol. Phys.*, **35**, 1713 (1978).

Table XIV. Total energy, atomization energy, geometry, and spectroscopic constants of Si₂ (¹Σ_g⁺).

Basis sets	t.e. (a.u.)	a.e. (eV)	R _e (Å)	ω _e (cm ⁻¹)	B _e (cm ⁻¹)	κ _e (dyn/cm)
STO-3G ^a	-570.92605	-0.173	1.868	922	0.344	0.703E+06
STO-3G* ^a	-571.00304	1.641	1.834	970	0.357	0.779E+06
MINI-1	-574.61832	-1.39	2.207	575	0.246	0.274E+06
SMIDI-3	-576.43889	-1.49	2.164	550	0.256	0.250E+06
MIDI-1	-574.70886	-1.32	2.132	565	0.264	0.264E+06
MIDI-3	-576.44799	-1.34	2.134	564	0.264	0.263E+06
MIDI-1*	-574.77919	-0.504	2.070	613	0.280	0.311E+06
MIDI-3*	-576.48793	-0.533	2.069	611	0.280	0.309E+06
Extended ^b	-577.63827	-0.563	2.068	609	0.281	0.307E+06
Exptl. ^c		3.20	2.246	511	0.239	0.216E+06

^a See footnote a to Table XIII.^b Since no extended basis set calculation was available, we performed a calculation on Si₂ by using the basis set consisting of (531111/4211) by Dunning¹⁰ plus one *d*-type polarization function, the exponent of which was taken from Table II.^c See footnote e to Table III.

There are alarmingly large differences between the standard atomic exponents and the corresponding standard molecular exponents for valence shell orbitals of Na, Mg, and Si in Pople's STO-3G basis sets. The free atom values are 1.31

(Na), 1.27 (Mg), and 1.53 (Si), while the values recommended for use in molecular calculations are 1.75 (Na), 1.70 (Mg), and 1.75 (Si).⁷ The value for Na was obtained by averaging the optimum exponents for NaH and NaCl. Both are ionic molecules and therefore the standard molecular expo-

Table XV. Total energy, atomization energy, and geometry of MgH₂ (¹Σ⁺).

Basis sets ^a	t.e. (a.u.)	a.e. (eV)	R _e (Å)
STO-3G ^b	-197.91062		1.483
STO-3G* ^b	-197.99340		1.546
(MINI-1)/MINI-1	-199.40184	-1.38	1.561
(MINI-1)/(MINI-1) ^c	-199.40578	-1.27	1.558
(MINI-1)/MIDI-1	-199.40684	-1.29	1.557
MIDI-1/MIDI-1	-199.54095	2.36	1.674
MIDI-1/MIDI-3	-200.18665	2.35	1.673
MIDI-1/MIDI-3*	-200.24276	2.98	1.714
(MINI-1*)/MIDI-1*	-199.56797	2.20	1.634
MIDI-1*/MIDI-1*	-199.60205	3.13	1.699
MIDI-1*/MIDI-3*	-200.24792	3.12	1.697
Extended ^d	-200.72051	3.394	1.709
Exptl.		---	---

^a See footnotes b and c to Table III.^b See footnote a to Table XIII.^c Optimized scale factor for 3s of Mg (1.079) was used for this calculation, where scale factor for H was taken to be 1.188.^d R. Ahlrichs, F. Keil, H. Lischka, W. Kutzelnigg, and V. Staemmler, *J. Chem. Phys.*, **63**, 455 (1975).**Table XVI.** Total energy, atomization energy, and geometry of SiH₄ (¹A₁).^a

Basis sets ^b	t.e. (a.u.)	a.e. (eV)	R _e (Å)
STO-3G	-287.91728	15.91	1.421
STO-3G*	-287.97186	17.26	1.423
(MINI-1)/MINI-1	-289.64198	8.69	1.537
MIDI-1/SMIDI-3	-290.58412	9.51	1.486
(MINI-1)/MIDI-1	-289.70970	9.33	1.479
MIDI-1/MIDI-1	-289.71833	9.57	1.484
MIDI-1/MIDI-3	-290.58695	9.54	1.485
MIDI-1/MIDI-3*	-290.63263	10.60	1.491
(MINI-1*)/MIDI-3*	-289.78643	10.90	1.483
MIDI-1*/MIDI-1*	-289.78648	10.90	1.490
MIDI-1*/MIDI-3*	-290.64006	10.80	1.490
Extended		10.97 ^c	---
Exptl.		13.3 ^c	1.480 ^d

^a See footnote a to Table III.^b See footnotes b and c to Table III.^c See footnote c to Table VI.^d D. R. J. Boyd, *J. Chem. Phys.*, **23**, 922 (1955).

Table XVII. Total energy, atomization energy, and geometry of ClF_3 (1A_1).^a

Basis sets ^b	t.e. (a.u.)	a.e. (eV)	$R_{e,\text{unq.}}$ (Å)	$R_{e,\text{eq.}}$ (Å)	θ (deg)
STO-3G	-748.24352	-7.02	1.791	1.787	77.8
44-31G	-756.58402	-5.00	1.714	1.815	84.2
STO-3G*	-748.49623	-0.26	1.650	1.662	83.7
MINI-1	-753.34655	-6.56	1.787	1.838	80.5
SMIDI-3	-755.83446	-5.27	1.711	1.798	82.8
MIDI-1	-753.59309	-4.81	1.688	1.783	83.4
MIDI-3	-755.87738	-4.90	1.690	1.781	83.4
SMIDI-3/MIDI-3*	-755.95488	-2.35	1.627	1.703	85.4
MIDI-3*	-756.01378	-1.46	1.591	1.678	85.6
Extended	---	---	---	---	---
Exptl. ^c		5.42	1.598	1.698	87.5

^a See footnote a to Table III.^b See footnote c to Table III.^c Geometry is taken from D. F. Smith, *J. Chem. Phys.*, 21, 609 (1953).

nent, 1.75, may not work well for molecules such as Na_2 . In fact, the value produced a large error (-26.6%) for Na_2 . As for NaH and MgH_2 , the optimum values of H are 0.76 (NaH) and 0.85 (MgH_2), while the standard value chosen by Pople is 1.24.⁷ Not surprisingly, the value produced large errors for NaH (-12.3%) and MgH_2 (-13.2%).

STO-3G basis sets have been used extensively for molecules consisting of lighter atoms with considerable success. However, it must be pointed out that the majority of the applications involve neutral hydrocarbon molecules and the related systems with some heteroatoms up to F, and crucial to the success was undoubtedly the rescaling process of the orbital exponent scales in the molecular environment. There existed a fortunate situation that optimum values of the scale factors over selected sample molecules were not terribly scattered from one molecule to another. Such a fortunate situation does not seem to exist for molecules in which the third-row atoms, Na through Cl, are involved. We have just discussed the cases where H, Na, Mg, and Si are involved. While conducting an intensive study of various basis sets, we have come to the decision that we should move toward abandonment of the idea of the so-called standard exponents. As a matter of

fact, we have decided to use orbital exponent parameters determined by atomic calculations without any change or rescaling when brought to molecular environments. The only exception is the hydrogen in MINI-1.

The ClF_3 molecule seems to present a tough test for Pople's basis sets. The experimental R_e are 1.598 Å ($\text{Cl}-\text{F}_{\text{unq.}}$) and 1.698 Å ($\text{Cl}-\text{F}_{\text{eq.}}$), while corresponding values from STO-3G are 1.791 and 1.787 Å, thus failing to predict even the relative order of the lengths. STO-3G* manages to correct the situation but only barely, namely 1.650 Å ($\text{Cl}-\text{F}_{\text{unq.}}$) and 1.662 Å ($\text{Cl}-\text{F}_{\text{eq.}}$). 44-31G fares better, i.e., 1.714 and 1.815 Å, respectively, but the agreement with the experimental values is not impressive. As shown in Table XVIII, none of our basis sets fails to predict the relative order of the two Cl-F bonds. Especially satisfying is the performance of MIDI-1*, which gives 1.591 Å ($\text{Cl}-\text{F}_{\text{unq.}}$) and 1.678 Å ($\text{Cl}-\text{F}_{\text{eq.}}$).

The results given by MIDI-1 seem to be better than those of 44-31G. 44-31G is larger in size than MIDI-1 as a basis set; it contains 12 *s*-type and 8 *p*-type primitive GTOs, while there are 9 *s*-type and 6 *p*-type primitive GTOs in MIDI-1. It is suspected that the well-known constraints, $\zeta_{2s} = \zeta_{2p}$ and $\zeta_{3s} = \zeta_{3p}$, imposed on 44-31G basis functions

Table XVIII. Calculated molecular geometries with various kinds of basis sets (bond lengths in Å, angles in deg, errors in %).^a

	Exptl. ^b	MINI-1	SMIDI-3	MIDI-1	SMIDI-3/ MIDI-3*	MIDI-1*	STO-3G	44-31G	STO-3G*
Bond lengths									
NaH	1.887	1.776(-5.9)	1.875(-0.6) ^d	1.875(-0.6)	1.926(2.1)	1.892(0.3)	1.654(-12.3)		1.725(-8.6)
NaCl	2.361	2.403(1.8)	2.391(1.3)	2.386(1.1)	2.356(-0.2) ^e	2.352(-0.4)	2.221(- 5.9)		2.175(-7.9)
MgH ₂ ^c	1.709	1.561(-8.7)	1.673(-2.1) ^d	1.674(-2.0)	1.714(0.3)	1.699(-0.6)	1.483(-13.2)		1.546(-9.5)
AlF	1.655	1.666(0.7)	1.672(1.0)	1.664(0.5)	1.653(-0.1)	1.638(-1.0)	1.616(- 2.4)		1.563(-5.6)
AlCl	2.130	2.303(8.1)	2.290(7.5)	2.252(5.7)	2.173(2.0) ^e	2.171(1.9)	2.164(1.6)		2.078(-2.4)
SiH ₄	1.480	1.537(3.9)	1.486(0.4)	1.484(0.3)	1.491(0.7)	1.490(0.7)	1.421(-4.0)		1.423(-3.9)
P ₂	1.894	2.020(6.7)	1.980(4.5)	1.928(1.8)	1.871(-1.2) ^e	1.871(-1.2)	1.808(-4.5)	1.949(2.9)	1.756(-7.3)
H ₂ S	1.328	1.413(6.4)	1.355(2.0)	1.351(1.7)	1.345(1.3)	1.343(1.1)	1.329(0.1)	1.354(2.0)	1.318(-0.8)
SO ₂	1.432	1.659(15.9)	1.575(10.0)	1.523(6.4)	1.454(1.5)	1.437(0.3)	1.562(9.1)	1.531(6.9)	1.446(1.0)
HCl	1.275	1.363(6.9)	1.308(2.6)	1.297(1.7)	1.284(0.7)	1.278(0.2)	1.313(3.0)	1.299(1.9)	1.287(0.9)
ClF	1.628	1.741(6.9)	1.721(5.7)	1.702(4.5)	1.658(1.8)	1.627(-0.1)	1.677(3.0)	1.714(5.3)	1.615(-0.8)
ClF ₃ (unq.)	1.598	1.787(11.8)	1.711(7.1)	1.688(5.6)	1.627(1.8)	1.591(-0.4)	1.791(12.1)	1.714(7.3)	1.650(3.3)
(eq.)	1.698	1.838(8.2)	1.798(5.9)	1.783(5.0)	1.703(0.3)	1.678(-1.2)	1.787(5.2)	1.815(6.9)	1.662(-2.1)
Cl ₂	1.986	2.184(10.0)	2.190(10.3)	2.188(10.2)	2.020(1.7) ^e	2.021(1.8)	2.063(3.9)	2.177(9.6)	1.967(-1.0)
Na ₂	3.079	3.230(4.9)	3.194(3.7) ^d	3.199(3.9)	3.227(4.8)	3.235(5.1)	2.259(-26.6)		2.652(-13.9)
Si ₂	2.246	2.207(-1.7)	2.164(-3.7)	2.132(-5.1)	2.069(-7.9) ^e	2.070(-7.8)	1.868(-16.8)		1.834(-18.3)
Mean of Error		6.8	4.3	3.5	1.8	1.5	7.7	5.3	5.4
(except Na ₂ , Si ₂)		7.3	4.4	3.4	1.1	0.8	5.7	5.3	3.9
Bond Angles									
H ₂ S	92.2	94.7(2.7)	95.8(3.9)	95.8(3.9)	93.8(1.7)	93.8(1.7)	92.5(0.3)	95.6(3.7)	91.8(-0.4)
SO ₂	119.5	108.6(-9.1)	112.8(-5.6)	115.9(-3.0)	118.7(-0.7)	118.1(-1.2)	109.2(-8.6)	115.1(-3.7)	119.9(0.3)
ClF ₃	87.5	80.5(-8.0)	82.8(-5.4)	83.4(-4.7)	85.4(-2.4)	85.6(-2.2)	77.8(-11.1)	84.2(-3.8)	83.7(-4.3)
Mean of Error		6.6	5.0	3.9	1.6	1.7	6.7	3.7	1.7

^a Values in parentheses are the errors calculated with eq. (1). The errors of bond angles have been calculated with a similar equation.

^b Experimental values were taken from *JANAF Thermochemical Tables, 2nd ed.*, D. R. Stull and H. Prophet, Eds., U.S. Department of Commerce, Washington, DC, 1971, except for SiH₄. D. R. J. Boyd, *J. Chem. Phys.*, **23**, 922 (1955) [SiH₄].

^c No experimental data are available for MgH₂, so that the value calculated with extended basis set is given instead (see Table XV).

^d The values obtained with MIDI-3 are shown here because no SMIDI-*i* basis set is defined for Na and Mg.

^e If molecules do not contain any H and second-row atoms, the values obtained with MIDI-3* are given.

for economical reasons seems to cost some numerical accuracy. Close examination of the data collected in Table XVIII and exhibited graphically in Figs. 1 and 2 should be enough to convince us that the general performance of MIDI-1 is appreciably better than that of 44-31G.

Finally, we shall discuss the Si₂ molecule, which seems to present another difficult case for STO-3G and STO-3G* as seen in Table XVIII. What is disturbing also for our basis sets is that even with our "best" basis set—MIDI-1*—the error remains rather high, i.e., -7.8%. If Na₂ and Si₂ are excluded, the average of absolute values of percentage

errors is as low as 0.8% for MIDI-1*. Since no extended basis set calculation was available for Si₂, we decided to perform a benchmark calculation. The basis set consists of (531111/4211) by Dunning¹⁰ plus one *d*-type polarization function, the exponent of which was taken from Table II. This extended basis set gives 2.068 Å, which is very close to 2.069 Å (MIDI-3*) and 2.070 Å (MIDI-1*). This result confirms our expectation that our good basis sets should yield computed molecular quantities close to those given by near Hartree-Fock calculations, with the exception of the total energy.

Calculated bond angles are also summarized in

Table XIX. Mean absolute percent error of calculated spectroscopic constants for diatomic molecules (in %).^a

	MINI-1	SMIDI-3	MIDI-1	SMIDI-3/MIDI-3*	MIDI-3*	Extended
[B_e]						
Error A	9.9	7.5	6.6	4.6	4.1	4.2
Error B	12.1	8.5	6.7	2.6	2.5	---
[ω_e]						
Error A	7.3	5.4	7.0	8.7	9.4	9.0
Error B	6.9	6.6	5.7	3.1	2.4	---
[κ_e]						
Error A	15.3	10.8	14.5	18.7	20.1	19.3
Error B	13.8	11.4	11.5	6.0	4.9	---

^a Error A = $[\sum_{i=1}^N (|Q_i^{\text{expt}} - Q_i^{\text{cal}}|/Q_i^{\text{expt}}) \times 100]/N$ (%), $N = 10$ except for extended basis set and $N = 8$ for extended basis set. Error B = $[\sum_{i=1}^N (|Q_i^{\text{extended}} - Q_i^{\text{cal}}|/Q_i^{\text{extended}}) \times 100]/N$ (%), $N = 8$, because no extended calculation is available for Na_2 and AlCl , where Q_i denotes the values of B_e , ω_e or κ_e of atom i , which are given in Tables III–XVII.

Table XVIII. MIDI-1 improves the results to a large extent for SO_2 and ClF_3 , while the result becomes slightly worse for H_2S compared with that of MINI-1. 44-31G gives almost the same bond angles as MIDI-1. STO-3G* gives good agreement with experiment for H_2S and SO_2 . However, it gives rather large errors for ClF_3 . As was seen in R_e values, the values of θ_e are improved generally from MINI-1 to MIDI-1 and from MIDI-1 to SMIDI-3/MIDI-3*. SMIDI-3/MIDI-3* gives almost the same results as MIDI- i^* and the calculated bond angles with these basis sets are very close to the experimental values. Then we may conclude that it is important to add a polarization function, at least to the basis sets of the third-row atoms in the molecules, in order to predict bond angles properly.

B. Spectroscopic Constants

Spectroscopic constants (ω_e , B_e , and κ_e) have been calculated for the diatomic molecules. The results are shown in Tables II, IV, and VII–XIV. Two kinds of error analysis have been carried out: (A) the error is defined by the deviation from the corresponding experimental value, (B) the error is measured from the value of the extended cal-

culation. Both of the errors are given in percent, and the mean absolute percentage errors, averaged over all data available, are given in Table XIX. They are named error A and error B.

Let us discuss B_e first. B_e is related to R_e as $B_e \propto 1/(\mu R_e^2)$, where μ is the reduced atomic mass. The extended calculation usually gives good agreement with the experiment for B_e as it does for R_e . The mean absolute percent error (error A) for extended basis set is 4.2% including Si_2 , 2.7% excluding Si_2 . It may be seen in Table XIX that both error A and error B are reduced by going from MINI- i through MIDI- i^* , and the results for SMIDI- i /MIDI- i^* and MIDI- i^* have almost the same quality as those of the extended calculations even for Si_2 .

The constants ω_e and κ_e are related to each other by $\kappa_e \propto \mu \omega_e^2$, and they describe the shape of the potential curve of a molecule near the equilibrium nuclear distance. It is to be noted that the extended basis set calculations do not give good agreement with experiment. Error A for the extended basis set is even larger than those of MINI-1 for both ω_e and κ_e . The large errors occur in P_2 , AlF , FCl , and Si_2 . It seems difficult to simulate precisely experimental potential curves by single-configuration Hartree–Fock SCF calcula-

Table XX. Orbital energies of SO₂ (¹A₁) (in a.u.).^a

Basis sets ^b	1a ₁	1b ₂	2a ₁	3a ₁	2b ₂	1b ₁	4a ₁	5a ₁
STO-3G ^c	-91.0010	-20.2001	-20.2001	-8.8806	-6.5126	-6.5104	-6.5093	-1.3148
MINI-1	-91.6537	-20.4119	-20.4119	-9.2239	-6.8743	-6.8724	-6.8712	-1.3892
(MINI-1)	-91.5272	-20.4326	-20.4327	-9.1243	-6.7714	-6.7699	-6.7682	-1.4066
(MINI-3)	-92.0561	-20.5753	-20.5754	-9.1546	-6.7736	-6.7722	-6.7705	-1.4072
(MINI-4)	-92.0287	-20.5608	-20.5608	-9.1658	-6.8450	-6.8436	-6.8418	-1.4072
MIDI-1	-91.7212	-20.5135	-20.5136	-9.2249	-6.8817	-6.8780	-6.8770	-1.4836
MIDI-3	-92.2481	-20.6187	-20.6187	-9.2574	-6.8858	-6.8822	-6.8811	-1.4877
MIDI-4	-92.1421	-20.6382	-20.6382	-9.2305	-6.9142	-6.9100	-6.9094	-1.5022
SMIDI-3/MIDI-3*	-92.2243	-20.6113	-20.6113	-9.2177	-6.8476	-6.8435	-6.8422	-1.5038
(MINI-1*)	-91.6147	-20.5018	-20.5016	-9.1432	-6.7958	-6.7938	-6.7914	-1.4720
(MINI-3*)	-92.1176	-20.6161	-20.6160	-9.1709	-6.7942	-6.7923	-6.7900	-1.4720
(MINI-4*)	-92.0825	-20.5988	-20.5987	-9.1827	-6.8642	-6.8625	-6.8601	-1.4799
MIDI-1*	-91.7179	-20.5127	-20.5127	-9.1830	-6.8412	-6.8393	-6.8371	-1.4947
MIDI-3*	-92.2204	-20.6120	-20.6120	-9.2088	-6.8380	-6.8360	-6.8338	-1.4969
MIDI-4*	-92.1296	-20.5852	-20.5852	-9.1974	-6.8813	-6.8790	-6.8772	-1.5043
Extended ^d	-92.1962	-20.6179	-20.6179	-9.1633	-6.8534	-6.8521	-6.8501	-1.5094

Basis sets	3b ₂	6a ₁	4b ₂	7a ₁	2b ₁	5b ₂	1a ₂	8a ₁
STO-3G	-1.2070	-0.7742	-0.4949	-0.5131	-0.4847	-0.3482	-0.2593	-0.3167
MINI-1	-1.2973	-0.9221	-0.6022	-0.6183	-0.5871	-0.4850	-0.4094	-0.4588
(MINI-1)	-1.3069	-0.8904	-0.5983	-0.6167	-0.5866	-0.4731	-0.4189	-0.4461
(MINI-3)	-1.3092	-0.8962	-0.5985	-0.6163	-0.5855	-0.4738	-0.4198	-0.4483
(MINI-4)	-1.3102	-0.9075	-0.6106	-0.6300	-0.5981	-0.4916	-0.4403	-0.4660
MIDI-1	-1.3756	-0.8962	-0.6505	-0.6620	-0.6332	-0.5131	-0.4575	-0.4719
MIDI-3	-1.3774	-0.8971	-0.6477	-0.6608	-0.6329	-0.5077	-0.4532	-0.4688
MIDI-4	-1.3920	-0.9135	-0.6710	-0.6836	-0.6500	-0.5385	-0.4841	-0.4980
SMIDI-3/MIDI-3*	-1.3998	-0.8621	-0.6634	-0.6725	-0.6436	-0.5143	-0.4872	-0.4717
(MINI-1*)	-1.3692	-0.8575	-0.6584	-0.6658	-0.6385	-0.5043	-0.4833	-0.4616
(MINI-3*)	-1.3706	-0.8618	-0.6576	-0.6642	-0.6365	-0.5035	-0.4820	-0.4620
(MINI-4*)	-1.3767	-0.8714	-0.6731	-0.6811	-0.6534	-0.5220	-0.5005	-0.4813
MIDI-1*	-1.3873	-0.8594	-0.6764	-0.6769	-0.6472	-0.5160	-0.4911	-0.4685
MIDI-3*	-1.3902	-0.8620	-0.6753	-0.6751	-0.6454	-0.5140	-0.4892	-0.4672
MIDI-4*	-1.3945	-0.8700	-0.6891	-0.6909	-0.6596	-0.5291	-0.5052	-0.4856
Extended	-1.4036	-0.8692	-0.6983	-0.6956	-0.6663	-0.5396	-0.5158	-0.4915

tions for these molecules. However, the SMIDI- i /MIDI- i^* and MIDI- i^* basis sets can simulate the results of the extended calculations fairly well except for AlF, the error of MIDI-1* for AlF being 9.9 and 20.8% for ω_e and κ_e , respectively. The values of error B in Table XIX include these data.

C. Total Energies and Atomization Energies

Total energies and atomization energies have been calculated at the computed geometries and the results are given in Tables III–XVIII. These tables show that the total energies given by MINI-1 are much lower than those of STO-3G and STO-3G*, while the number of primitive GTOs used in MINI-1 is the same as that of STO-3G. The MIDI-4 sets give almost comparable total energies with 44-31G. For P₂, MIDI-4 gives even slightly lower energy than 44-31G.

Atomization energies have been calculated by subtracting the molecular total energies from the sum of the atomic energies. The data of atomic energies for the second-row atoms are given in a previous article,¹ and those of the third-row atoms are given in Table XXII. It may be seen in Tables III–XVII that the MINI- i basis sets give the smallest atomization energies among all basis sets used except for Cl₂, and for 8 of 15 molecules the MINI- i sets give negative atomization energies. The split basis sets usually show considerable amount of improvement. Although 7 of 15 molecules still have negative values, their absolute values become small except for Cl₂.

The role of the polarization functions is very substantial in the calculation of atomization energies for the molecules under consideration. Both MINI- i^* and MIDI- i^* usually give reasonable values for atomization energies. MIDI-1*, MIDI-3*, and MIDI-4* give essentially the same values of atomization energies and the values are

close to those given by the extended calculations. It is to be noted that the values will converge in going from MIDI-3* to MIDI-4*. However, they still decrease from MINI-3* to MINI-4*. Generally, $i = 1$ basis sets give the largest atomization energies among $i = 1, 3$, and 4 basis sets of the same group. It might be due to the accumulation of errors because of the “softness” of the inner part of the basis sets, which implies the lack of sufficiently large exponents.

Pople et al.⁶ calculated the atomization energies by using STO-3G, 44-31G, and STO-3G* and compared them with the experimental values. Their conclusion was that STO-3G* gave the best agreement with experiment. However, this agreement does not always hold. The value is too large for NaCl and NaH in Tables VII and IX, while it is too small for ClF₃ in Table XVII compared with experimental values. The values given by STO-3G* are always larger than those given by extended calculations. One possible source of large atomization energies given by STO-3G* may be that these values were obtained by subtracting the total molecular energy from the sum of the atomic energies calculated with molecule-optimized scale factors rather than with atom-optimized scale factors. In addition, there might be the basis set superposition error or the accumulation of other errors because of the “softness” of the inner-core part of STO-3G*. The 44-31G basis sets give very close values of atomization energies to those given by the MIDI- i basis sets. However, the values obtained by 44-31G were obtained in the same way as with STO-3G*. If one subtracts the total molecular energy from the sum of the atomic energies calculated, not with molecular-optimized scale factors but with atom-optimized scale factors, the calculated atomization energies for 44-31G should become smaller.

After all, it has been well documented that the single-configuration Hartree–Fock calculation

Footnotes to Table XX

^a The values were calculated at the optimized geometries, which are given in Table V, except for those of the extended calculation.

^b See footnotes b and e to Table III.

^c We performed the calculation by using STO-3G given in ref. 7.

^d See ref. 11; the values were calculated at the experimental geometry.

Table XXI. The time spent by the CPU of AMDAHL 470V/6 computer for SO₂ (in sec).

Basis sets	Integral	SCF	Total
MINI-1	13.2	2.8	16
MINI-3	15.4	2.8	18
MINI-4	21.2	2.9	24
SMIDI-3	19.4	6.1	26
SMIDI-3/MIDI-3	20.3	6.6	27
MIDI-1	20.6	10.8	31
MIDI-3	23.0	10.4	33
MIDI-4	28.5	11.9	40
SMIDI-3/MIDI-3*	60.6	13.9	75
MINI-1*	151.3	12.7	164
MINI-3*	163.8	12.4	176
MINI-4*	224.5	12.5	237
MIDI-1*	179.9	36.6	217
MIDI-3*	192.9	37.2	230
MIDI-4*	253.0	45.4	298

always gives considerably smaller molecular bindings compared with the experimental values. Our consolation comes from the observation that the MIDI-*i** basis sets give atomization energies which are close to those given by extended basis set calculations.

D. Orbital Energies

In Table XX, the orbital energies of SO₂ calculated with various kinds of basis sets are given for illustration. Those values have been obtained at the optimized geometries, which are given in Table V, except for those of the extended calculation. The values for the extended basis sets are taken from Huzinaga and Yoshimine,¹¹ which are calculated at the experimental geometry, $R_e = 1.4321$ Å, $\theta = 119.54^\circ$. The calculated geometry with the same basis sets is $R_e = 1.423$ Å, $\theta = 118.4^\circ$.

It is found in Table XX that the orbital energies given by MINI-*i* are much closer to the extended ones than those of STO-3G, especially for the valence orbitals. The split basis sets MIDI-*i* give better orbital energies than the corresponding MINI-*i*, and the effect of splitting seems to be essential for the valence orbitals. The addition of the polarization functions brings further improvement

to the higher orbital energies. The SMIDI-*i*/MIDI-*i**, the MINI-*i**, and the MIDI-*i** sets can reproduce the orbital ordering of $1a_2$ and $8a_1$ given by the extended calculation, while it is still difficult to reproduce the subtle difference in the orbital ordering of $4b_2$ and $7a_1$. The SMIDI-3/MIDI-3* sets can give almost the same orbital energies as MIDI-3*. The values given by the $i = 1$ and the $i = 3$ basis set are slightly worse than $i = 4$ basis sets for each kind of basis set, MINI-*i*, MIDI-*i*, MINI-*i**, and MIDI-*i**. As was mentioned in the preceding article, the $i = 1$ and the $i = 3$ basis sets, where p_1 consists of three primitive Gaussian functions, give rather poor atomic valence p orbital energies for the second-row atoms, while they give satisfactory agreement with DZ values for the third-row atom. Therefore, a combined basis set SMIDI-4/MIDI-3* would be recommended for use in reproducing the results of the extended calculation.

IV. CONCLUDING REMARKS

The STO-3G and the 4-31G basis sets have been used extensively for molecular calculations, especially for molecules consisting of hydrogen and the second-row atoms. However, these basis sets are not so successful for the molecules that contain the third-row atoms. The flexibility of the basis sets seems to be much required in the molecular calculation containing third-row atoms.

The following points have emerged from our computational observations so far: (i) The idea of standard molecular scale factor does not work well for molecules containing the third-row atoms. (ii) The splitting of valence orbitals is necessary and essential for the molecules treated in the present work. (iii) Addition of polarization functions to split basis sets can yield computed bond lengths and bond angles generally in close agreement with experiment. The spectroscopic constants and the atomization energies given by these basis sets always agree fairly well with the values given by near Hartree-Fock calculations.

Finally, let us summarize these findings by recommending appropriate basis sets for *ab initio* molecular calculations.

As for the simplest usable basis sets, SMIDI-1

Table XXII. Atomic total energies given by SMIDI-3, MIDI-*i*, MINI-*i**, and MIDI-*i** (*i* = 1, 3, and 4) (in a.u.).^a

	Na	Mg	Al	Si	P	S	Cl	Ar
SMIDI-3	---	---	-241.34305	-288.24678	-340.03038	-396.72051	-458.59584	-525.81896
MIDI-1	-160.87701	-198.46040	-240.59025	-287.37875	-339.03987	-395.59812	-457.33410	-524.41054
MIDI-3	-161.42284	-199.10651	-241.34428	-288.24859	-340.03281	-396.72382	-458.59992	-525.82393
MIDI-4	-161.62363	-199.33970	-241.57169	-288.50367	-340.31681	-397.04444	-458.95843	-526.22621
MINI-1*	-160.88914	-198.49114	-240.57066	-287.35892	-339.01605	-395.57333	-457.30472	-524.37599
MINI-3*	-161.43542	-199.13874	-241.31463	-288.21476	-339.99174	-396.67810	-458.54559	-525.76094
MINI-4*	-161.62694	-199.34551	-241.56752	-288.50027	-340.31419	-397.04289	-458.95791	-526.22624
MIDI-1*	-160.88969	-198.49305	-240.60612	-287.39885	-339.06614	-395.62883	-457.37025	-524.45386
MIDI-3*	-161.43568	-199.13943	-241.34851	-288.25375	-340.03924	-396.73145	-458.60881	-525.83424
MIDI-4*	-161.62723	-199.34622	-241.57592	-288.50882	-340.32324	-397.05264	-458.96726	-526.23686

^a Atomization energies have been calculated by subtracting the molecular total energy from the sum of the atomic total energies given in this table. The values for MINI-*i* are given in the preceding article. As for H, the value used is -0.49698 a.u. for all of MINI-1, MIDI-1, MINI-1*, and MIDI-1*. The values for O and F were taken from ref. 1 except for SMIDI-3. The values for SMIDI-3 of O and F are -74.62938 and -99.14411 a.u., respectively.

^b Atomic total energies for MINI-*i** and MIDI-*i** have been obtained as follows: For Na and Mg, a *p*-type polarization function has been used, so that the atomic total energies for MINI-*i** and MIDI-*i** have been recalculated by adding the *p*-type function with the exponent given in Table II to the original MINI-*i* and MIDI-*i*. As for Al through Ar, a *d*-type polarization function has been augmented. The program used for the molecular calculation used six-membered *d*-type Gaussian functions $(x^2, y^2, z^2, xy, yz, zx)e^{-\gamma r^2}$. They contain one 3*s*-type function, $(x^2 + y^2 + z^2)e^{-\gamma r^2} = r^2e^{-\gamma r^2}$, in addition to five genuine *d*-type functions. Therefore, in order to be consistent in the computation of atomization energies, the reference atomic energies have been recalculated by taking into account these additional 3*s* Gaussian functions. The exponents used are given in Table II. The effects are quite sizable if the original atomic orbital bases are rather small.

and SMIDI-1/MIDI-1 would be recommended for use in a wide range of molecular calculations. The latter one may give almost the same results as MIDI-1, because the splitting of the *s*-type valence orbital is less important for B through Ne compared with Al through Ar. If we are interested in energy, the *i* = 3 or the *i* = 4 basis sets might be preferred because of the "hardness" of the inner-core basis sets, although the *i* = 4 basis sets are slightly time-consuming as is seen in Table XXI.

As for the basis sets augmented with polarization functions, use of the MIDI-3* sets would be recommended, and if a molecule contains second-row atoms, SMIDI-3/MIDI-3* are also useful basis sets. As is shown in Table XXI, by using SMIDI-3/MIDI-3*, we can reduce the computer time by a large amount compared with MIDI-3* sets.

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