

# A Systematic Preparation of New Contracted Gaussian-Type Orbital Sets. III. Second-Row Atoms from Li through Ne

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Four minimal Gaussian basis sets are generated for the second-row atoms Li through Ne. The first one, MINI-1, consists of a 3-term contraction of primitive Gaussian-type orbitals for 1s, 2s, and 2p atomic orbitals. The convenient shorthand notation would be (3,3) for Li-Be and (3,3/3) for B-Ne. The second one, MINI-2, can be represented by (3,3/4) for B-Ne. In the same way, MINI-3 is described as (4,3) for Li-Be, and MINI-3 and MINI-4 are represented by (4,3/3) and (4,3/4) for B-Ne, respectively. Although the four basis sets are the minimal type, they give the valence shell orbital energies which are close to those of DZ. These four and other sets derived from them are tested for the hetero- and homodiatomic molecules and some organic molecules. They are found to give the orbital energies that agree well with those given by extended calculations. Atomization energies and other spectroscopic constants are also calculated and compared with those of extended calculations. The results clearly indicate that the present basis sets can be used very effectively in the molecular calculations.

## 1. INTRODUCTION

Gaussian-type atomic SCF functions were originally proposed to break the bottleneck of many-center integrals<sup>1</sup> in quantum chemistry. The Gaussian-type functions have become powerful tools for investigating molecular electronic structure.

There is, however, a grave drawback in using Gaussian-type functions. Because of their inadequate functional forms in the vicinity of the nucleus, many Gaussians tend to be spent for the innermost orbitals at the expense of an adequate description of outer orbitals. Some sophisticated contraction methods have been developed,<sup>2,3</sup> but they have not been totally successful in avoiding this drawback.

The STO-KGs given by Pople's group, which used *K* Gaussians for each orbital with different quantum numbers,<sup>4,5</sup> places uniform emphasis

over the entire electron distribution in atoms.

Furthermore, Ditchfield, Hehre, and Pople<sup>6</sup> have developed new sets from Li to F where the uniform emphasis on the charge distributions is held, but the exponents and coefficients of each contracted Gaussian-type orbital (CGTOs) are determined so as to give the minimum energy. They made two types of sets, with and without the constraint that the exponents of 2s ( $\zeta_{2s}$ ) equal those of 2p ( $\zeta_{sp}$ ). Tavouktsoglou and Huzinaga<sup>7</sup> have given almost the same basis sets. The difference between the two is that the former authors determined the coefficients of CGTOs by treating them as nonlinear parameters and using the pattern search technique of Hook and Jeeves,<sup>8</sup> and the latter authors determined the coefficients through the SCF procedure. Hehre, Ditchfield, and Pople<sup>9</sup> and Hehre et al.<sup>10</sup> tested only the constrained basis sets and found that their basis sets do not describe the molecular environment as well.

The Tavouktsoglou and Huzinaga<sup>7</sup> method was refined by the present authors<sup>11</sup> and applied to the transition metal atoms from Sc to Zn. The basis sets and their derivatives were tested by SCF cal-

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**Table I.** Total energies and orbital energies (a.u.).

	Li	Be	B	C
<b>Total energies</b>				
SZ <sup>a</sup>	-7.41848	-14.55674	-24.49837	-37.62239
MINI-1	-7.37809	-14.47611	-24.37273	-37.45282
MINI-2	—	—	-24.37708	-37.46766
MINI-3	-7.41926	-14.54929	-24.48652	-37.61626
MINI-4	—	—	-24.49089	-37.63112
MIDI-1	-7.38080	-14.48199	-24.38290	-37.46657
MIDI-2	—	—	-24.38727	-37.48147
MIDI-3	-7.41994	-14.55064	-24.48879	-37.61972
MIDI-4	—	—	-24.49316	-37.63457
4-31G <sup>b</sup>	—	—	-24.49426	-37.63595
DZ <sup>a</sup>	-7.43272	-14.57237	-24.52792	-37.68675
HF <sup>a</sup>	-7.43273	-14.57302	-24.52906	-37.68861
<b>1s orbital energies</b>				
SZ <sup>a</sup>	-2.46019	-4.71712	-7.67787	-11.30156
MINI-1	-2.45057	-4.68612	-7.62572	-11.22740
MINI-2	—	—	-7.62365	-11.22458
MINI-3	-2.47073	-4.72127	-7.68006	-11.30394
MINI-4	—	—	-7.67833	-11.30117
MIDI-1	-2.45517	-4.69594	-7.64010	-11.24496
MIDI-2	—	—	-7.63813	-11.24212
MIDI-3	-2.47283	-4.72539	-7.68575	-11.31127
MIDI-4	—	—	-7.68398	-11.30844
4-31G <sup>b</sup>	—	—	-7.67625	-11.29941
DZ <sup>a</sup>	-2.47768	-4.73283	-7.69943	-11.32343
HF <sup>a</sup>	-2.47773	-4.73267	-7.69533	-11.32554
<b>2s orbital energies</b>				
SZ <sup>a</sup>	-0.19489	-0.30864	-0.48391	-0.67750
MINI-1	-0.19557	-0.30818	-0.49205	-0.69959
MINI-2	—	—	-0.49236	-0.70143
MINI-3	-0.19607	-0.30889	-0.49336	-0.70181
MINI-4	—	—	-0.49369	-0.70348
MIDI-1	-0.19560	-0.30826	-0.49184	-0.69912
MIDI-2	—	—	-0.49212	-0.70086
MIDI-3	-0.19609	-0.30895	-0.49329	-0.70160
MIDI-4	—	—	-0.49359	-0.70323
4-31G <sup>b</sup>	—	—	-0.49103	-0.70016
DZ <sup>a</sup>	-0.19632	-0.30923	-0.49408	-0.70436
HF <sup>a</sup>	-0.19632	-0.30927	-0.49469	-0.70563
<b>2p orbital energies</b>				
SZ <sup>a</sup>	—	—	-0.30038	-0.40162
MINI-1	—	—	-0.30416	-0.42255
MINI-2	—	—	-0.30851	-0.43090
MINI-3	—	—	-0.30392	-0.42207
MINI-4	—	—	-0.30842	-0.43047
MIDI-1	—	—	-0.30495	-0.42333
MIDI-2	—	—	-0.30942	-0.43168
MIDI-3	—	—	-0.30432	-0.42248
MIDI-4	—	—	-0.30883	-0.43089
4-31G <sup>b</sup>	—	—	-0.30851	-0.42963

**Table I** (continued from previous page)

	Li	Be	B	C
DZ <sup>a</sup>	—	—	−0.30989	−0.43263
HF <sup>a</sup>	—	—	−0.30986	−0.43335
Total energies				
	N	O	F	Ne
SZ <sup>a</sup>	−54.26824	−74.54037	−98.94211	−127.81218
MINI-1	−54.06244	−74.33922	−98.77655	−127.71879
MINI-2	−54.09601	−74.40480	−98.88801	−127.89218
MINI-3	−54.28496	−74.62938	−99.14411	−128.17268
MINI-4	−54.31860	−74.69504	−99.25567	−128.34616
MIDI-1	−54.08350	−74.36550	−98.81192	−127.76241
MIDI-2	−54.11719	−74.43130	−98.92358	−127.93606
MIDI-3	−54.28986	−74.63593	−99.15255	−128.18329
MIDI-4	−54.32348	−74.70160	−99.26408	−128.35670
4-31G <sup>b</sup>	−54.32529	−74.70244	−99.26418	---
DZ <sup>a</sup>	−54.39795	−74.80432	−99.40131	−128.53511
HF <sup>a</sup>	−54.40092	−74.80937	−99.40930	−128.54705
1s orbital energies				
SZ <sup>a</sup>	−15.59378	−20.61394	−26.30293	−32.66213
MINI-1	−15.49520	−20.49515	−26.15743	−32.49239
MINI-2	−15.48998	−20.48734	−26.15152	−32.48618
MINI-3	−15.60034	−20.63022	−26.33066	−32.70607
MINI-4	−15.59565	−20.62400	−26.32511	−32.70015
MIDI-1	−15.51888	−20.52287	−26.19166	−32.53235
MIDI-2	−15.51370	−20.51511	−26.18600	−32.52639
MIDI-3	−15.60953	−20.64118	−26.34350	−32.72097
MIDI-4	−15.60461	−20.63482	−26.33796	−32.71503
4-31G <sup>b</sup>	−15.59534	−20.62294	−26.32226	---
DZ <sup>a</sup>	−15.62541	−20.66258	−26.37363	−32.75988
HF <sup>a</sup>	−15.62909	−20.66866	−26.38273	−32.77248
2s orbital energies				
SZ <sup>a</sup>	−0.89254	−1.15089	−1.43065	−1.73250
MINI-1	−0.93526	−1.22742	−1.54586	−1.89320
MINI-2	−0.93866	−1.23363	−1.55735	−1.90991
MINI-3	−0.93827	−1.23137	−1.55140	−1.90036
MINI-4	−0.94157	−1.23779	−1.56264	−1.91665
MIDI-1	−0.93446	−1.22640	−1.54448	−1.89156
MIDI-2	−0.93772	−1.23243	−1.55585	−1.90809
MIDI-3	−0.93796	−1.23088	−1.55075	−1.89955
MIDI-4	−0.94114	−1.23721	−1.56198	−1.91583
4-31G <sup>b</sup>	−0.93777	−1.23179	−1.55366	---
DZ <sup>a</sup>	−0.94316	−1.24045	−1.56651	−1.92187
HF <sup>a</sup>	−0.94531	−1.24433	−1.57254	−1.93043
2p orbital energies				
SZ <sup>a</sup>	−0.50336	−0.50327	−0.52641	−0.56172
MINI-1	−0.54961	−0.60227	−0.68516	−0.78889
MINI-2	−0.56310	−0.62409	−0.71802	−0.83370
MINI-3	−0.54907	−0.60124	−0.68427	−0.78781
MINI-4	−0.56271	−0.62341	−0.71717	−0.83261

**Table I** (continued from previous page)

	Li	Be	B	C
MIDI-1	-0.55044	-0.60297	-0.68577	-0.78944
MIDI-2	-0.56392	-0.62471	-0.71856	-0.83415
MIDI-3	-0.54950	-0.60162	-0.68460	-0.78811
MIDI-4	-0.56311	-0.62373	-0.71748	-0.83288
4-31G <sup>b</sup>	-0.56163	-0.62157	-0.71364	—
DZ <sup>a</sup>	-0.56587	-0.62827	-0.72391	-0.84143
HF <sup>a</sup>	-0.56758	-0.63192	-0.73001	-0.85044

<sup>a</sup> See ref. 13.<sup>b</sup> Using the exponents and coefficients given by Ditchfield, Hehre, and Pople<sup>14</sup> and Hehre and Pople,<sup>15</sup> we have recalculated total energies and orbital energies. Total energies given here are different from those given in refs. 14 and 15 (see text).

culations on the Cu<sub>2</sub> molecule and the results were encouraging.<sup>12</sup> No constraints such as  $\zeta_{3s} = \zeta_{3p}$  are imposed in these calculations.

This article presents eight new Gaussian basis sets which belong to the same vein of the basis sets in refs. 11 and 12, for second-row atoms. Four of these basis sets correspond to the standard set (1) [STD-SET (1)], double-zeta class set (1) [DZC-SET (1)], split STD-SET (1) [SSTD-SET (1)], and split DZC-SET [SDZC-SET (1)] of refs. 11 and 12. This article includes an application of the basis sets to some molecules. The constraints such as  $\zeta_{2s} = \zeta_{2p}$  are not imposed here.

## 2. ATOMIC WAVEFUNCTIONS

### A. MINI-1, MINI-2, MINI-3, and MINI-4

In a minimal basis set, 1s, 2s, and 2p orbitals from Li through Ne are expressed by

$$\phi_{1s} = C_{1s,1}s_1 + C_{1s,2}s_2 \quad (1)$$

$$\phi_{2s} = C_{2s,1}s_1 + C_{2s,2}s_2 \quad (2)$$

$$\phi_{2p} = p_1 \quad (3)$$

The functions  $s_1$ ,  $s_2$ , and  $p_1$  may be chosen arbitrarily. If these functions are single Slater-type orbitals, we call them single zeta (SZ). In the present work, each orbital is expanded by different Gaussian-type orbital (GTO) sets  $\{G(s_1)\}$ ,  $\{G(s_2)\}$ , and  $\{G(2p)\}$ .

First we prepare four minimal-type basis sets, MINI-1, MINI-2, MINI-3, and MINI-4. The primitive GTOs for MINI-1 are 3, 3, and 3 for the  $s_1$ ,  $s_2$ , and  $p_1$  orbitals. The shorthand description is (3,3/3). The primitive GTOs for MINI-2, MINI-3,

and MINI-4 are (3,3/4), (4,3/3), and (4,3/4), respectively. The expansion coefficients and the exponents of the Gaussians are determined for  $s_1$ ,  $s_2$ , and  $p_1$  to give the optimum energy, except for MINI-2 where  $s_1$  and  $s_2$  have the same primitive Gaussians as MINI-1 but the expansion coefficients of these orbitals are reoptimized. [We rename STD-SET (1) and DZC-SET (1) in ref. 11 as MINI-1 and MINI-2, respectively.]

The total energies and orbital energies are given in Table I together with those from other calculations, SZ, DZ, HF,<sup>13</sup> 4-31G,<sup>14,15</sup> MIDI-1, MIDI-2, MIDI-3, and MIDI-4 (the meanings of the last four will be explained in Sec. 2 B). It is seen from Table I that the difference between the total energies of SZ and MINI-1 starts with 0.04 a.u. at Li and reaches maximum at N and O (ca. 0.20 a.u.) and then decreases. We note that the orbital energy difference between the two calculations for the 1s increases as the nuclear charge increases. Therefore, the relatively better total energies for the heavier atoms are the result of the improvement in the valence orbitals (this is discussed below). In MINI-2, the total energy of Ne surpasses the result of SZ. The total energies calculated by MINI-3 are lower than those found by SZ except for Be, B, and C, and the energies found by MINI-4 are lower than those of SZ except for B.

The errors defined by

$$\text{Error} = |\epsilon_{\text{HF}} - \epsilon_i| / |\epsilon_{\text{HF}}| \dots \quad (4)$$

where  $i$  = MINI-1, MINI-2, MINI-3, MINI-4, 4-31G, and DZ and  $\epsilon$  is the orbital energy, are shown in Figures 1(a)–1(c).

The errors defined by eq. (4) for SZ are 0.7–0.3% for the inner orbital 1s, and those for MINI-1 are

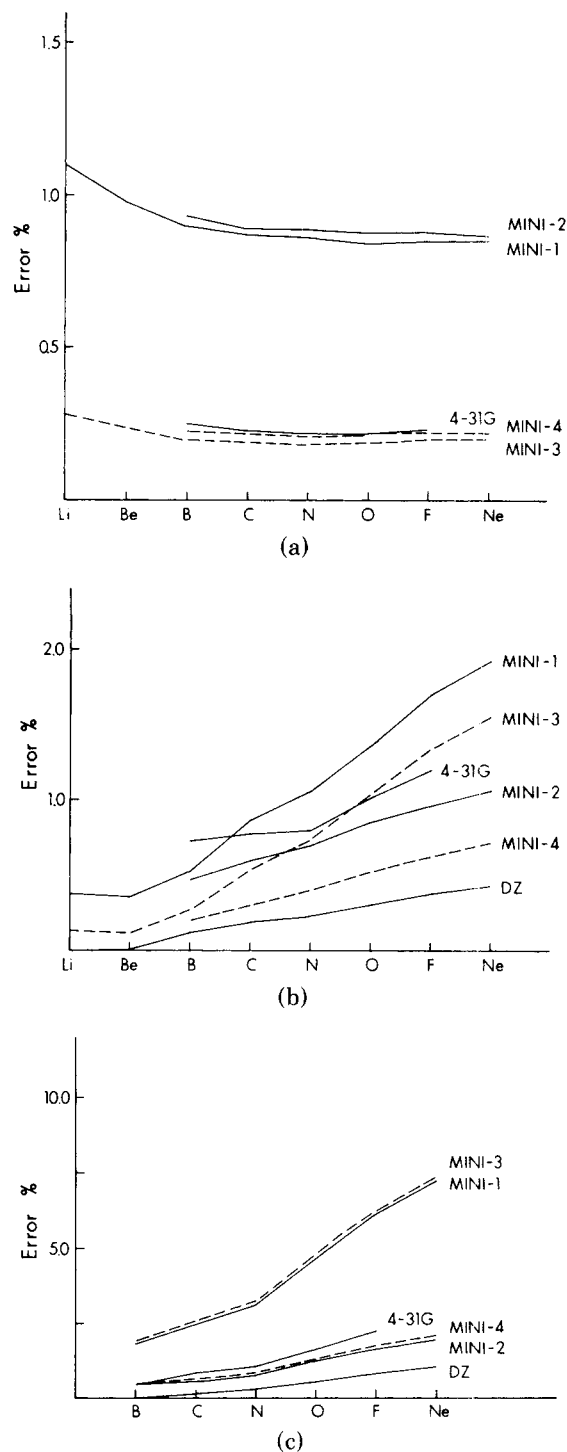
1.1–0.9%. On the other hand, the errors of the valence orbitals of SZ are worse than those of MINI-1; in SZ the error increases from 0.7% (Li) to 10.3% (Ni) for 2s and from 3.1% (B) to 34% (Ne) for 2p, and they decrease to only 0.4–1.9% for 2s and 1.8–7.2% for 2p in MINI-1. Proceeding from MINI-1 (33/3) to MINI-2 (33/4), one may find that extra *p* Gaussian ameliorates 2s orbital energy as well as 2p orbital energy [see Figs. 1(b) and 1(c)]. The errors of 2p decrease to 0.1–1.9%, which are quite close to those of DZ. The addition of extra Gaussian to *s*<sub>1</sub> of MINI-1 and MINI-2 improves the orbital energies of 1s and 2s appreciably [see Figs. 1(b) and 1(c)], whereas the addition of an extra *s*-type Gaussian has virtually no effect on those of 2p. The improvement in the 1s orbital energy contributes to the decrease in the total energies of MINI-3 and MINI-4.

The expansion coefficients and orbital exponents are given in Table II. Although we allowed the expansion coefficients of *s*<sub>1</sub> and *s*<sub>2</sub> to vary in MINI-2, it was found that they remained at the same values of *s*<sub>1</sub> and *s*<sub>2</sub> in MINI-1 for B, C, N, and O.

## B. MIDI-1, MIDI-2, MIDI-3, and MIDI-4

The main components of the outer shells *s*<sub>2</sub> and *p*<sub>1</sub> are split into two parts, one consisting of *n* – 1 primitive GTOs (*s*<sub>2</sub>' and *p*<sub>2</sub>') and the other of one primitive GTO (*s*<sub>2</sub>'' and *p*<sub>2</sub>''). Varying the exponents of *s*<sub>2</sub>' when *s*<sub>1</sub> is expanded in three primitive Gaussians we have found that *s*<sub>2</sub>' is used to describe the 1s orbital, and as a result *s*<sub>2</sub> is almost completely represented by *s*<sub>2</sub>'. This result is not appropriate for the present aim of finding good atomic orbitals for molecular calculations. Therefore, we decided not to optimize split orbitals with respect to total atomic energies. By partitioning *s*<sub>2</sub> and *p*<sub>2</sub> of MINI-1, MINI-2, MINI-3, and MINI-4 into *s*<sub>2</sub>', *s*<sub>2</sub>'', *p*<sub>2</sub>', and *p*<sub>2</sub>'', we create four new basis sets, MIDI-1, MIDI-2, MIDI-3, and MIDI-4, whose results are given in Table I.

In Table I it is seen that the splitting of *s*<sub>2</sub> and *p*<sub>2</sub> ameliorates the orbital energies of 1s for MIDI-1 and MIDI-2, whereas the effect of the splitting is relatively small for MIDI-3 and MIDI-4. The 1s cores described by MINI-3 and MINI-4 are less affected by the changes in the outer shells than those by MINI-1 and MINI-2. Similarly, the 1s cores of MIDI-3 and MIDI-4 are expected to be more solid and more firm than



**Figure 1.** Error of the orbital energies for (a) 1s, (b) 2s, and (c) 2p.

those of MIDI-1 and MIDI-2. The effect of splitting on the valence orbitals for all the basis sets under consideration is minimal. It is also seen in Table I that the total energies produced by MIDI-4 are approximately equal to those produced by 4-

**Table II.** Exponents and expansion coefficients for MINI-1, MINI-2, MINI-3, and MINI-4.

	Li	Be	B	C	N	O	F	Ne
<b>Exponents for MINI-1</b>								
$s_1$	35.04615	66.95354	108.43704	153.17226	218.36449	281.86658	368.37112	456.95285
	5.20169	9.93929	16.12056	23.07303	32.59889	42.41600	55.06106	68.36543
	1.05624	2.05713	3.37343	4.92329	6.91739	9.09562	11.74767	14.61976
$s_2$	0.71517	1.91221	3.56650	5.72557	8.32638	11.46603	15.15184	19.32719
	0.07053	0.16132	0.29547	0.45504	0.65919	0.88786	1.15137	1.44182
	0.02735	0.05524	0.09805	0.14707	0.21009	0.27880	0.35811	0.44408
$p_1$	—	—	2.57207	4.25131	6.12035	8.04724	10.57707	13.35252
	—	—	0.51694	0.86327	1.25938	1.66842	2.19498	2.77947
	—	—	0.12314	0.20135	0.29145	0.37251	0.47937	0.60097
<b>Expansion coefficients for MINI-1</b>								
$s_1$	0.07376	0.07020	0.06865	0.07074	0.06787	0.06906	0.06704	0.06691
	0.39747	0.39191	0.38993	0.39538	0.39020	0.39316	0.38925	0.38935
	0.66509	0.66997	0.67139	0.66331	0.67008	0.66567	0.67079	0.67052
$s_2$	-0.09397	-0.08282	-0.08242	-0.08138	-0.08089	-0.08082	-0.08055	-0.08025
	0.57010	0.55755	0.55907	0.57485	0.56720	0.58209	0.58773	0.59530
	0.49975	0.51604	0.51680	0.50241	0.51109	0.49716	0.49198	0.48487
$p_1$	—	—	0.10590	0.10993	0.11592	0.12427	0.12627	0.12884
	—	—	0.45718	0.46271	0.46996	0.47659	0.47795	0.48044
	—	—	0.63186	0.62751	0.61845	0.61304	0.61401	0.61167

	B	C	N	O	F	Ne
<b>Exponents for MINI-2<sup>a</sup></b>						
$p_1$	6.05234	9.46891	13.58077	17.74107	22.75387	28.44672
	1.24788	2.00766	2.92452	3.86540	4.99353	6.28149
	0.33732	0.54643	0.79829	1.04796	1.34957	1.69649
	0.09555	0.15185	0.21875	0.27578	0.34770	0.43202
<b>Expansion coefficients for MINI-2</b>						
$s_1$	0.06865 <sup>b</sup>	0.07074 <sup>b</sup>	0.06787 <sup>b</sup>	0.06906 <sup>b</sup>	0.06703	0.06690
	0.38993	0.39538	0.39020	0.39316	0.38909	0.38917
	0.67140	0.66331	0.67008	0.66567	0.67094	0.67069
$s_2$	-0.08242	-0.08138	-0.08089	-0.08082	-0.08067	-0.08039
	0.55906	0.57485	0.56720	0.58209	0.58824	0.59605
	0.51679	0.50241	0.51109	0.49716	0.49149	0.48414
$p_1$	0.03496	0.03785	0.03968	0.04279	0.04458	0.04591
	0.19634	0.20843	0.21620	0.22797	0.23483	0.23961
	0.50515	0.50867	0.51039	0.50883	0.50873	0.50901
	0.48138	0.46978	0.46309	0.46135	0.45885	0.45599

	Li	Be	B	C	N	O	F	Ne
<b>Exponents for MINI-3</b>								
$s_1$	104.72613	193.43735	308.87663	451.88826	621.69096	819.40889	1043.07203	1295.45250
	15.66225	29.03932	46.44522	67.99899	93.58744	123.38598	157.11479	195.11433
	3.39955	6.38974	10.30154	15.14702	20.90772	27.62522	35.24041	43.80814
	0.85039	1.64101	2.68144	3.96983	5.50386	7.29598	9.33063	11.61688

**Table II** (continued from previous page)

	Li	Be	B	C	N	O	F	Ne
$s_2$	0.75753	1.90163	3.44029	5.39688	7.77526	10.58719	13.81518	17.46717
	0.06590	0.15889	0.29461	0.46686	0.67624	0.92731	1.21569	1.54138
	0.02529	0.05357	0.09601	0.14875	0.21194	0.28733	0.37333	0.46988
$p_1$	—	—	2.56914	4.21807	6.10393	8.07753	10.55923	13.32538
	—	—	0.51667	0.85846	1.25715	1.67368	2.19220	2.77542
	—	—	0.12301	0.20046	0.29092	0.37310	0.47863	0.60003
Expansion coefficients for MINI-3								
$s_1$	0.02011	0.01977	0.01959	0.01943	0.01933	0.01924	0.01919	0.01912
	0.13752	0.13558	0.13472	0.13400	0.13359	0.13313	0.13292	0.13264
	0.45714	0.45787	0.45855	0.45909	0.45964	0.45975	0.46004	0.46020
	0.53469	0.53205	0.53027	0.52936	0.52853	0.52834	0.52785	0.52770
$s_2$	−0.09166	−0.08406	−0.08418	−0.08356	−0.08297	−0.08306	−0.08294	−0.08274
	0.64701	0.58668	0.58027	0.57272	0.56713	0.56755	0.56613	0.56446
	0.41987	0.48847	0.49830	0.50785	0.51482	0.51559	0.51786	0.52018
$p_1$	—	—	0.10638	0.11103	0.11643	0.12386	0.12660	0.12920
	—	—	0.45795	0.46415	0.47068	0.47627	0.47840	0.48081
	—	—	0.63096	0.62538	0.61748	0.61382	0.61343	0.61113

	B	C	N	O	F	Ne
Exponents for MINI-4						
$s_1$	308.88024	451.90190	621.71806	821.83934	1044.02406	1295.58161
	46.44338	67.99577	93.58168	123.68182	157.21281	195.10741
	10.30027	15.14423	20.90232	27.66617	35.24628	43.79454
	2.68081	3.96843	5.50117	7.29957	9.32771	11.60971
$s_2$	3.44091	5.40077	7.78145	10.60696	13.83395	17.49415
	0.29355	0.46395	0.67090	0.91764	1.20268	1.52322
	0.09551	0.14736	0.20942	0.28317	0.36776	0.46227
$p_1$	6.03322	9.47460	13.58580	17.75037	22.74336	28.44174
	1.24581	2.00714	2.92376	3.86468	4.99043	6.27937
	0.33699	0.54621	0.79806	1.04772	1.34908	1.69636
	0.09542	0.15171	0.21858	0.27560	0.34749	0.43189
Expansion coefficients for MINI-4						
$s_1$	0.01959	0.01943	0.01933	0.01917	0.01916	0.01911
	0.13472	0.13400	0.13358	0.13281	0.13282	0.13262
	0.45857	0.45910	0.45967	0.45946	0.45997	0.46020
	0.53027	0.52937	0.52854	0.52901	0.52807	0.52776
$s_2$	−0.08412	−0.08349	−0.08288	−0.08293	−0.08284	−0.08265
	0.58328	0.57839	0.57420	0.57659	0.57583	0.57512
	0.49536	0.50233	0.50797	0.50670	0.50835	0.50972
$p_1$	0.03520	0.03790	0.03974	0.04281	0.04466	0.04596
	0.19728	0.20895	0.21671	0.22833	0.23521	0.23988
	0.50551	0.50882	0.51054	0.50884	0.50864	0.50886
	0.48022	0.46929	0.46259	0.46111	0.45864	0.45595

<sup>a</sup> The exponents for  $s_1$  and  $s_2$  are fixed to those of MINI-1 of this table. Only the expansion coefficients for these orbitals are varied.

<sup>b</sup> The expansion coefficients for  $s_1$  and  $s_2$  remain the same as those of MINI-1.

**Table III.** Definition of basis sets and expansion terms.<sup>a</sup>

	Li-Be	B-Ne
MINI-1	(3,3)	(3,3/3)
MINI-2	—	(3,3/4)
MINI-3	(4,3)	(4,3/3)
MINI-4	—	(4,3/4)
MIDI-1	(3,(2,1))	(3,(2,1)/(2,1))
MIDI-2	—	(3,(2,1)/(3,1))
MIDI-3	(4,(2,1))	(4,(2,1)/(2,1))
MIDI-4	—	(4,(2,1)/(3,1))
MAXI-1		
.		
.		
.		
MAXI-M		

<sup>a</sup> The numbers in parentheses represent the expansion terms of each contracted Gaussian-type orbital. The symbol  $(N-1,1)$  means outer orbitals, which are expanded by  $N$  terms in the MINI series and are split into two parts, one containing  $N-1$  terms and the other one term. A slash separates the different symmetries.

31G. [The total energies from 4-31G in this article are different from those given by Pople's group<sup>14,15</sup> because their method is unrestricted Hartree-Fock and does not give the energy of a pure state while our method is symmetry and spin restricted<sup>16</sup> (see footnote b to Table I).]

### C. MAXI-1, MAXI-2 . . .

The names MAXI-1, MAXI-2 . . . MAXI-N might be suitable for other splittings of the present

basis sets. The relationships between the names and expansion terms are summarized in Table III.

## 3. ORBITAL ENERGIES AND ATOMIZATION ENERGIES OF DIATOMIC MOLECULES

### A. Orbital Energies

The eight basis sets—MINI- $i$  and MIDI- $i$  ( $i = 1, 2, 3$  and  $4$ )—are examined by SCF calculations on homo- and heteronuclear diatomic molecules. The exponents of the outer shells  $2s$  and  $2p$  are optimized in the first four basis sets. The resulting scaling factors are given in Table IV. No serious differences of the scaling factors in each atom are observed. The basis sets are then augmented with a polarization function of  $p$  type for H, Li, and Be and of  $d$  type for B through Ne. The exponent of the polarization function is determined by maximizing the overlap defined as

$$\text{OVLP} = \{n_s \langle 2s | \text{polarization} \rangle + n_p \langle 2p | \text{polarization} \rangle\} / (n_s + n_p) \quad (5)$$

where  $\langle i | \text{polarization} \rangle$  indicates the radial overlap integral of an orbital  $i$ , and the polarization function and  $n_s$  and  $n_p$  are the numbers of electrons in the  $2s$  and  $2p$  orbitals. We used the  $s_2$  and  $p_1$  orbitals of MINI-1 and determined the exponents for the polarization functions; these are given in Table V. The energetically optimized polarization functions are discussed in the Appendix. The orbital energies calculated by various sets for the

**Table IV.** Optimum scale factors of MINI-1, MINI-2, MINI-3, and MINI-4 for diatomic molecules.<sup>a</sup>

	MINI-1		MINI-2		MINI-3		MINI-4	
	2s	2p	2s	2p	2s	2p	2s	2p
H <sup>b</sup>	1.188	—	—	—	1.189	—	—	—
Li	1.026	—	—	—	1.016	—	—	—
Be	1.013	—	—	—	1.009	—	—	—
B <sup>c</sup>	0.992	1.202	0.990	1.259	0.987	1.209	0.985	1.266
C	1.050	1.050	1.054	1.055	1.043	1.053	1.048	1.056
N	1.017	1.061	1.019	1.060	1.011	1.063	1.014	1.061
O <sup>d</sup>	1.017	1.024	1.018	1.014	1.011	1.025	1.012	1.015
F	1.011	1.005	1.010	1.003	1.005	1.006	1.006	1.004
Ne	1.008	0.999	1.007	0.999	1.002	1.000	1.002	1.000

<sup>a</sup> The scaling factors are determined by calculations of homopolar diatomic molecules except for B and O.

<sup>b</sup> The value given is optimum for  $1s$ . See footnote d in Table XI.

<sup>c</sup> The optimum scaling factors are determined by calculating the BF molecule where the scaling factors of F are fixed to those given in this table.

<sup>d</sup> The optimum scaling factors are determined by calculating the CO molecule where the scaling factors of C are fixed to those given in this table.



**Table V.** Exponents of polarization functions.

	H	Li	Be	B	C	N	O	F	Ne
p.f. <sup>a</sup>	2 <i>p</i>	2 <i>p</i>	2 <i>p</i>	3 <i>d</i>	3 <i>d</i>	3 <i>d</i>	2 <i>d</i>	3 <i>d</i>	3 <i>d</i>
exponent	0.68 <sup>b</sup>	0.07	0.16	0.40	0.61	0.87	1.16	1.50	1.89

<sup>a</sup> p.f. = polarization functions.

<sup>b</sup> The method discussed in this article gives the value of 0.48. In many molecules, the 1*s* orbital of H is contracted compared with the atomic 1*s*. We multiplied (1.188)<sup>2</sup> given in Table IV with the value of 0.48 obtained by the method given in the text. Note that the other scaling factors in Table IV are around 1.0.

molecules C<sub>2</sub>, N<sub>2</sub>, F<sub>2</sub>, Ne<sub>2</sub>, and CO are given in Tables VI–X. The basis sets augmented with the polarization function are indicated by an asterisk to the original sets. The equilibrium nuclear distances adopted are those of Cade and Wahl for the homonuclear diatomics<sup>17</sup> and those of McLean and Yoshimine for the heteronuclear diatomics.<sup>18</sup> From Tables VI–X we may deduce the following conclusions:

(1) The effect of using the least-energy-fitting basis sets . . . MINI-*i*: Comparing the MINI-*i* (*i* = 1, 2, 3, and 4) results with the SZ results one finds that the orbital energies of the valence orbitals by MINI-*i* are much closer to the extended ones than those of SZ.

(2) The effect of the splitting . . . MIDI-*i*: In many cases, the split sets MIDI-*i* (*i* = 1, 2, 3, and 4) yield better orbital energies than the corresponding minimal set MINI-*i*.

(3) The effect of the polarization function . . . MINI-*i*\* and MIDI-*i*\*: The added polarization functions bring further improvement for the higher orbital energies of MINI-*i*\* and MIDI-*i*\* compared with the corresponding orbital energies of MINI-*i* and MIDI-*i*. The agreement between the results of MIDI-4\* and the extended basis sets for almost all the orbitals and the agreement between the results of MIDI-2\* for the outer shells and those of the extended basis sets are satisfactory; however, we see below how the polarization functions contaminate the 1σ<sub>g</sub> and 1σ<sub>u</sub> orbital energies of F<sub>2</sub> and Ne<sub>2</sub> in the case of MINI-1\*, MINI-2\*, MIDI-1\*, and MIDI-2\*.

(4) The effect of extra Gaussian in *s*<sub>1</sub>: Comparing the results of BASE-*i* with those of BASE-*i* + 2 (BASE = MINI, MIDI, MINI\*, and MIDI\*), one finds that the increase in the expansion term of *s*<sub>1</sub> improves the lowest two orbital energies

**Table VI.** Summary of the orbital energies for C<sub>2</sub> (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)<sup>a</sup> (a.u.).

	1σ <sub>g</sub>	2σ <sub>g</sub>	1σ <sub>u</sub>	2σ <sub>u</sub>	1π <sub>u</sub>
SZ <sup>b</sup>	−11.36560	−1.03337	−11.36414	−0.48984	−0.43579
MINI-1	−11.27890	−1.06487	−11.28010	−0.50770	−0.45522
MINI-2	−11.28094	−1.07402	−11.28226	−0.51356	−0.46754
MINI-3	−11.35478	−1.06703	−11.35357	−0.51039	−0.45581
MINI-4	−11.35855	−1.07711	−11.35736	−0.51689	−0.46858
MIDI-1	−11.30085	−1.08661	−11.29847	−0.51188	−0.45381
MIDI-2	−11.29352	−1.08425	−11.29167	−0.51128	−0.46026
MIDI-3	−11.36665	−1.08908	−11.36431	−0.51405	−0.45302
MIDI-4	−11.35931	−1.08682	−11.35705	−0.51339	−0.45952
MINI-1*	−11.27529	−1.03687	−11.27614	−0.50595	−0.44261
MINI-2*	−11.27944	−1.04558	−11.28044	−0.51292	−0.45536
MINI-3*	−11.33339	−1.03813	−11.33189	−0.50728	−0.44220
MINI-4*	−11.33911	−1.04772	−11.33767	−0.51480	−0.45538
MIDI-1*	−11.30014	−1.05629	−11.29760	−0.51128	−0.44866
MIDI-2*	−11.29843	−1.05785	−11.29589	−0.51308	−0.45622
MIDI-3*	−11.35236	−1.05926	−11.35004	−0.51375	−0.44803
MIDI-4*	−11.35028	−1.06067	−11.34797	−0.51551	−0.45553
Extended <sup>c</sup>	−11.35980	−1.06127	−11.35749	−0.51724	−0.45788

<sup>a</sup> The calculated nuclear distance is 2.3481 a.u., which is given in ref. 17.

<sup>b</sup> The calculated nuclear distance is 2.3475 a.u. See ref. 33.

<sup>c</sup> See ref. 17.

**Table VII.** Summary of the orbital energies for  $N_2$  ( $^1\Sigma_g^+$ )<sup>a</sup> (a.u.).

	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$1\sigma_u$	$2\sigma_u$	$1\pi_u$
sz <sup>b</sup>	-15.72176	-1.45241	-0.54451	-15.71965	-0.73066	-0.57951
MINI-1	-15.56671	-1.48528	-0.57804	-15.56849	-0.75556	-0.61523
MINI-2	-15.56901	-1.49811	-0.59862	-15.57108	-0.76540	-0.63206
MINI-3	-15.67275	-1.48765	-0.57923	-15.67079	-0.75865	-0.61569
MINI-4	-15.67636	-1.50116	-0.60005	-15.67443	-0.76887	-0.63291
MIDI-1	-15.61222	-1.52782	-0.62154	-15.60893	-0.77191	-0.61788
MIDI-2	-15.59818	-1.52465	-0.62931	-15.59559	-0.76949	-0.62314
MIDI-3	-15.70173	-1.53053	-0.62058	-15.69811	-0.77449	-0.61648
MIDI-4	-15.68832	-1.52786	-0.62867	-15.68480	-0.77231	-0.62215
MINI-1*	-15.52598	-1.41738	-0.58245	-15.52788	-0.74629	-0.58320
MINI-2*	-15.53022	-1.43012	-0.60075	-15.53254	-0.75721	-0.60166
MINI-3*	-15.61071	-1.41880	-0.58198	-15.60831	-0.74820	-0.58235
MINI-4*	-15.61618	-1.43221	-0.60055	-15.61388	-0.75943	-0.60127
MIDI-1*	-15.59973	-1.46787	-0.61872	-15.59600	-0.76820	-0.60345
MIDI-2*	-15.59329	-1.47047	-0.62936	-15.58958	-0.77034	-0.61215
MIDI-3*	-15.67227	-1.47127	-0.61793	-15.66868	-0.77125	-0.60245
MIDI-4*	-15.66586	-1.47392	-0.62885	-15.66230	-0.77357	-0.61131
Extended <sup>c</sup>	-15.68195	-1.47360	-0.63495	-15.67883	-0.77796	-0.61544

<sup>a</sup> All the calculations are performed at  $R = 2.068$  a.u.<sup>b</sup> See ref. 33.<sup>c</sup> See ref. 17.

considerably and leaves the highest occupied orbitals in each symmetry almost unchanged.

(5) The effect of extra Gaussian in  $p_1$ : Comparing the orbital energies of BASE- $i$  with BASE- $i$  + 1 (BASE = MINI, MIDI, MINI\*, and MIDI\*),

one finds that the increase in the expansion term of  $p_1$  decreases most orbital energies except the first three lowest ones. Furthermore, we observe that the higher orbital energies of BASE- $i$  approach the corresponding counterparts of BASE- $i$

**Table VIII.** Summary of the orbital energies for  $F_2$  ( $^1\Sigma_g^+$ )<sup>a</sup> (a.u.).

	$1\sigma_g$	$2\sigma_g$	$3\sigma_g$	$1\sigma_u$	$2\sigma_u$	$1\pi_u$	$1\pi_g$
sz <sup>b</sup>	-26.38210	-1.63270	-0.55685	-26.38193	-1.36795	-0.61427	-0.47932
MINI-1	-26.19361	-1.74551	-0.70394	-26.19847	-1.47663	-0.77010	-0.62640
MINI-2	-26.19683	-1.76519	-0.73329	-26.20184	-1.49364	-0.80726	-0.66583
MINI-3	-26.37413	-1.75096	-0.70511	-26.37539	-1.48337	-0.77154	-0.62819
MINI-4	-26.37321	-1.76936	-0.73307	-26.37453	-1.49911	-0.80728	-0.66607
MIDI-1	-26.26237	-1.75463	-0.71279	-26.26234	-1.48620	-0.78142	-0.63903
MIDI-2	-26.24781	-1.76851	-0.73633	-26.24807	-1.49634	-0.81300	-0.67239
MIDI-3	-26.41363	-1.75989	-0.71157	-26.41342	-1.49273	-0.78006	-0.63763
MIDI-4	-26.39895	-1.77354	-0.73517	-26.39878	-1.50269	-0.81170	-0.67106
MINI-1*	-26.22868	-1.73764	-0.71122	-26.23612	-1.47538	-0.76821	-0.62436
MINI-2*	-26.23146	-1.75548	-0.74362	-26.23916	-1.49168	-0.80457	-0.66300
MINI-3*	-26.37943	-1.74206	-0.71060	-26.38091	-1.48092	-0.76782	-0.62396
MINI-4*	-26.37847	-1.75871	-0.74160	-26.38001	-1.49600	-0.80280	-0.66106
MIDI-1*	-26.28141	-1.74402	-0.71677	-26.28115	-1.48133	-0.77600	-0.63302
MIDI-2*	-26.26653	-1.75579	-0.74373	-26.26627	-1.49057	-0.80659	-0.66523
MIDI-3*	-26.41058	-1.75010	-0.71586	-26.41036	-1.48874	-0.77472	-0.63157
MIDI-4*	-26.39538	-1.76182	-0.74299	-26.39516	-1.49797	-0.80547	-0.66393
Extended <sup>c</sup>	-26.42268	-1.75653	-0.74603	-26.42243	-1.49498	-0.80522	-0.66289

<sup>a</sup> All the calculations are performed at  $R = 2.68$  a.u.<sup>b</sup> See ref. 33.<sup>c</sup> See ref. 17.

**Table IX.** Summary of the orbital energies for Ne<sub>2</sub> (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)<sup>a</sup> (a.u.).

	1σ <sub>g</sub>	3σ <sub>g</sub>	1σ <sub>u</sub>	3σ <sub>u</sub>	1π <sub>u</sub>	1π <sub>g</sub>
MINI-1	-32.47834	-0.81827	-32.47894	-0.74810	-0.78916	-0.77848
MINI-2	-32.47148	-0.86385	-32.47208	-0.79220	-0.83494	-0.82168
MINI-3	-32.69911	-0.81980	-32.69929	-0.74985	-0.79078	-0.78013
MINI-4	-32.69009	-0.86456	-32.69028	-0.79310	-0.83572	-0.82250
MIDI-1	-32.53077	-0.82376	-32.53123	-0.75317	-0.79432	-0.78369
MIDI-2	-32.52249	-0.86848	-32.52298	-0.79714	-0.83922	-0.82605
MIDI-3	-32.71977	-0.82255	-32.71983	-0.75190	-0.79306	-0.78240
MIDI-4	-32.71161	-0.86739	-32.71168	-0.79597	-0.83808	-0.82490
MINI-1*	-32.51263	-0.82065	-32.51451	-0.75022	-0.79141	-0.78070
MINI-2*	-32.50602	-0.86616	-32.50794	-0.79448	-0.83724	-0.82396
MINI-3*	-32.70312	-0.82031	-32.70339	-0.74998	-0.79110	-0.78041
MINI-4*	-32.69389	-0.86494	-32.69418	-0.79323	-0.83600	-0.82273
MIDI-1*	-32.55915	-0.82441	-32.55916	-0.75343	-0.79483	-0.78417
MIDI-2*	-32.55062	-0.86869	-32.55064	-0.79715	-0.83937	-0.82617
MIDI-3*	-32.72258	-0.82309	-32.72261	-0.75196	-0.79343	-0.78272
MIDI-4*	-32.71373	-0.86755	-32.71376	-0.79585	-0.83816	-0.82492
Extended <sup>b</sup>	-32.76701	-0.88420	-32.76701	-0.81329	-0.85489	-0.84060

<sup>a</sup> All the calculations are performed at  $R = 4.0$  a.u.<sup>b</sup> See ref. 34.

+ 2 proceeding from C<sub>2</sub>, N<sub>2</sub>, BF, F<sub>2</sub>, to Ne<sub>2</sub>. The expansion term  $p_1$  dominates the orbital energies for the molecules with heavy atoms.

We now discuss the effects of the polarization functions on the innermost orbitals. The 1σ<sub>g</sub> and 1σ<sub>u</sub> orbital energies of MINI-1\* and MINI-2\* for

F<sub>2</sub> and Ne<sub>2</sub> are fairly lower (ca. -0.035 a.u.) than those by MINI-1 and MINI-2. The similar results are found in the case of MIDI-1\* and MIDI-2\* for these molecules.

If the sizes of the basis sets are sufficiently large, the added polarization functions leave the lowest

**Table X.** Summary of the orbital energies for CO (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)<sup>a</sup> (a.u.).

	1σ	2σ	3σ	4σ	5σ	1π
sz <sup>b</sup>	-20.70597	-11.35323	-1.49881	-0.73234	-0.48078	-0.58308
MINI-1	-20.52211	-11.32670	-1.55082	-0.78127	-0.52727	-0.64419
MINI-2	-20.52289	-11.34809	-1.56501	-0.79719	-0.54700	-0.66295
MINI-3	-20.65518	-11.40444	-1.55453	-0.78364	-0.52935	-0.64478
MINI-3	-20.65710	-11.42734	-1.56904	-0.79980	-0.54950	-0.66382
MIDI-1	-20.56812	-11.31860	-1.56485	-0.79419	-0.54893	-0.63894
MIDI-2	-20.53849	-11.31997	-1.56156	-0.79910	-0.55359	-0.64725
MIDI-3	-20.68586	-11.38291	-1.56830	-0.79554	-0.54849	-0.63754
MIDI-4	-20.65630	-11.38530	-1.56535	-0.80050	-0.55368	-0.64616
MINI-1*	-20.53800	-11.29366	-1.50282	-0.78684	-0.52889	-0.62547
MINI-2*	-20.53780	-11.31386	-1.51537	-0.80300	-0.54794	-0.64453
MINI-3*	-20.64606	-11.35237	-1.50568	-0.78764	-0.52942	-0.62478
MINI-4*	-20.64658	-11.37369	-1.51863	-0.80423	-0.54875	-0.64423
MIDI-1*	-20.56978	-11.29914	-1.52265	-0.79733	-0.54260	-0.62930
MIDI-2*	-20.54253	-11.30089	-1.51801	-0.80096	-0.54962	-0.63688
MIDI-3*	-20.66942	-11.35031	-1.52661	-0.79851	-0.54249	-0.62788
MIDI-4*	-20.64279	-11.35238	-1.52220	-0.80238	-0.54991	-0.63580
Extended	-20.66430	-11.35972	-1.52097	-0.80383	-0.55437	-0.63947

<sup>a</sup> All the calculations are performed at  $R = 2.132$  a.u.<sup>b</sup> See ref. 33.<sup>c</sup> See ref. 18.

**Table XI.** Molecular total energies<sup>a</sup> and atomization energies (a.u.).

	H <sub>2</sub>		Li <sub>2</sub>		Be <sub>2</sub>	
	t.e.	a.e.	t.e.	a.e.	t.e.	a.e.
SZ or SZ + P	-1.1275	0.1275 <sup>b</sup>	(-14.84149 <sup>c</sup>	-0.0045)	(-29.05825 <sup>c</sup>	-0.0552)
MINI-1	-1.12206 <sup>d</sup>	0.1281	-14.75177	-0.0044	-28.86669	-0.0855
MINI-3	-1.12668 <sup>d</sup>	0.1281	-14.83375	-0.0048	-29.01253	-0.0861
MIDI-1	-1.12168	0.1277	-14.75705	-0.0046	-28.89231	-0.0717
MIDI-3	-1.12457	0.1260	-14.83538	-0.0045	-29.03023	-0.0711
MINI-1*	-1.12658	0.1326	-14.75904	0.0029	-28.89649	-0.0557
MINI-3*	-1.13085	0.1323	-14.84033	0.0018	-29.04079	-0.0578
MIDI-1*	-1.12511	0.1312	-14.76414	0.0025	-28.91880	-0.0452
MIDI-3*	-1.12854	0.1300	-14.84215	0.0023	-29.05588	-0.0454
Extended	-1.13363 <sup>e</sup>	0.1336	-14.87152 <sup>e</sup>	0.0061	-29.11751 <sup>e</sup>	-0.0285
	C <sub>2</sub>		N <sub>2</sub>		F <sub>2</sub>	
	t.e.	a.e.	t.e.	a.e.	t.e.	a.e.
SZ	-75.21122 <sup>c</sup>	-0.0336	-108.57362 <sup>c</sup>	0.0371	-197.87409 <sup>c</sup>	-0.0101
MINI-1	-74.86717	-0.0385	-108.13164	0.0068	-197.50551	-0.0476
MINI-2	-74.89889	-0.0364	-108.19505	0.0030	-197.70263	-0.0734
MINI-3	-75.18572	-0.0468	-108.56596	-0.0040	-198.23684	-0.0514
MINI-4	-75.21711	-0.0451	-108.62900	-0.0082	-198.43404	-0.0773
MIDI-1	-74.92673	-0.0064	-108.27363	0.1066	-197.57374	-0.0501
MIDI-2	-74.95745	-0.0055	-108.34158	0.1072	-197.77366	-0.0735
MIDI-3	-75.23173	-0.0077	-108.68456	0.1048	-198.25394	-0.0512
MIDI-4	-75.26158	-0.0076	-108.75144	0.1045	-198.45304	-0.0751
MINI-1*	-74.93208	0.0162	-108.28162	0.1425	-197.55156	-0.0270
MINI-2*	-74.96317	0.0175	-108.34007	0.1336	-197.75498	-0.0469
MINI-3*	-75.23747	0.0045	-108.69851	0.1282	-198.25220	-0.0368
MINI-4*	-75.26779	0.0051	-108.75610	0.1185	-198.45541	-0.0568
MIDI-1*	-74.97253	0.0258	-108.37227	0.1868	-197.61503	-0.0373
MIDI-2*	-75.00010	0.0234	-108.43379	0.1807	-197.82136	-0.0546
MIDI-3*	-75.26555	0.0254	-108.76624	0.1858	-198.26852	-0.0373
MIDI-4*	-75.29294	0.0231	-108.82769	0.1800	-198.47431	-0.0547
Extended	-75.40620 <sup>e</sup>	0.0290	-108.9928 <sup>e</sup>	0.1910	-198.7682 <sup>e</sup>	-0.0504
	Ne <sub>2</sub>		BF		CO	
	t.e.	a.e.	t.e.	a.e.	t.e.	a.e.
SZ	—	—	-123.61550 <sup>c</sup>	0.1750	-112.34357 <sup>c</sup>	0.1808
MINI-1	-255.43421	-0.0034	-123.31302	0.1637	-111.91818	0.1261
MINI-2	-255.77848	-0.0059	-123.41378	0.1487	-111.98777	0.1153
MINI-3	-256.34100	-0.0044	-123.78559	0.1550	-112.36177	0.1161
MINI-4	-256.68561	-0.0067	-123.88643	0.1399	-112.43075	0.1046
MIDI-1	-255.52258	-0.0022	-123.38857	0.1938	-112.05348	0.2214
MIDI-2	-255.86581	-0.0063	-123.48552	0.1747	-112.12860	0.2158
MIDI-3	-256.36412	-0.0025	-123.83207	0.1907	-112.47416	0.2185
MIDI-4	-256.70692	-0.0065	-123.92853	0.1713	-112.54837	0.2122
MINI-1*	-255.46632	-0.0009	-123.38719	0.2208	-112.05015	0.2438
MINI-2*	-255.81085	-0.0036	-123.49083	0.2084	-112.12379	0.2367
MINI-3*	-256.34210	-0.0041	-123.83416	0.2030	-112.47417	0.2280
MINI-4*	-256.68660	-0.0066	-123.93826	0.1911	-112.54682	0.2201
MIDI-1*	-255.55701	-0.0020	-123.44090	0.2257	-112.13697	0.2875
MIDI-2*	-255.90025	-0.0064	-123.54914	0.2177	-112.21484	0.2844
MIDI-3*	-256.36528	-0.0020	-123.86676	0.2247	-112.54274	0.2864
MIDI-4*	-256.70786	-0.0064	-123.97465	0.2166	-112.62040	0.2835
Extended	-257.0845 <sup>f</sup>	-0.0085	-124.16709 <sup>g</sup>	0.2287	-112.78911 <sup>g</sup>	0.2911

occupied orbital energies almost unchanged from that given by the original sets or make them slightly higher than those by the original sets. Some examples are found in the calculations for the  $\text{H}_2\text{O}$  and  $\text{N}_2$ ,<sup>19</sup>  $\text{FH}$ ,<sup>20</sup> and  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ .<sup>21</sup> The difference of  $\epsilon$  (with polarization function)  $-\epsilon$  (without polarization function) for the lowest orbitals is 0.001–0.003, 0.006–0.007, 0.027–0.029, –0.001 to +0.009 and –0.002 a.u. for  $\text{FH}$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$ , respectively.

The results for the orbital energies by MINI-1\*, MINI-2\*, MIDI-1\*, and MIDI-2\* for  $\text{F}_2$  and  $\text{Ne}_2$  suggest that the polarization functions in these basis sets were used partly to compensate insufficiency in the expansion terms of  $s_1$  and to decrease the atomic 1s energies. In order to analyze the situation properly, we must recognize and distinguish two different factors involved here. The first may be identified with the so-called basis set superposition error (BSSE),<sup>26–22</sup> which could show up whenever small, unsaturated basis sets are in use, with or without polarization functions. This is essentially an interatomic effect. The second factor is associated with the Cartesian forms of  $d$ -type or higher polarization functions. The problem arises when one uses a set of six  $d$ -type functions

$$(x^2, y^2, z^2, xy, yz, zx)e^{-\gamma r^2}$$

which actually contains one  $s$ -type function

$$(x^2 + y^2 + z^2)e^{-\gamma r^2} = r^2e^{-\gamma r^2}$$

as a redundancy. Therefore, when we use such a six-membered set of  $d$ -type polarization functions, we are actually adding a new  $s$ -type function whose effect would be dominantly *intra*-atomic. It is thus imperative to recalculate atomic energies with additional  $s$  functions whenever such  $d$ -type polarization functions are introduced to molecular

calculation. The atomic energies with this correction are given in the Appendix.

Comparing the 1s orbital energies given in Table I and Table XXIII, one may find that the inclusion of  $r^2e^{-\gamma r^2}$  leads to decreases in energy of 0.025–0.029 a.u. for F and Ne in MINI-1, MINI-2, MIDI-1, and MIDI-2. Hence, one may conclude that the surprisingly large energy decreases found in  $1\sigma_g$  and  $1\sigma_u$  in molecular calculations by using MINI-1\*, MINI-2\*, MIDI-1\*, and MIDI-2\* are mostly due to the atomic energy decreases brought by  $r^2e^{-\gamma r^2}$ . Similar tendencies are found in  $\text{Ne}_2$ .

Effects (1)–(5) above are closely related to the calculated spectroscopic constants.

## B. Atomization Energies

Table XI displays the total energies and atomization energies by MINI-1, MINI-2, . . . , MIDI-3\*, and MIDI-4\*. The atomization energy seems to be particularly suitable for discussing the characters of various basis sets. In  $\text{H}_2$ ,  $\text{Li}_2$ , and  $\text{Be}_2$ , MINI-1 and MINI-3 give nearly the same values. The same results are observed between MIDI-1 and MIDI-3 and so on. The increase of the expansion terms in  $s_1$  affects the atomization energies of these molecules only slightly.

We shall now discuss  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{F}_2$ ,  $\text{Ne}_2$ ,  $\text{BF}$ , and  $\text{CO}$ .

(i) MINI- $i$ : The use of the least-energy-fitting set MINI- $i$  ( $i = 1, 2, 3$ , and 4) leads to smaller atomization energies than SZ. We may say the atoms described by MINI- $i$  are harder than those described by SZ. We can classify the molecules into three groups: the first consisting of  $\text{C}_2$  and  $\text{N}_2$ , the second of  $\text{BF}$ ,  $\text{F}_2$ , and  $\text{Ne}_2$ , and the third of the CO molecule.

In the first group, the extra  $s$  Gaussian in  $s_1$  brings more changes in atomization energies than

### Footnotes to Table XI

<sup>a</sup> The calculated nuclear distances ( $R$ ) used in the present work are 1.4, 5.051, 4.0, 2.3481, 2.068, 2.68, and 4.0 a.u. for  $\text{H}_2$ ,  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ,  $\text{F}_2$ , and  $\text{Ne}_2$ . Except for  $\text{Ne}_2$ , the values are taken from ref. 17. For  $\text{BF}$  and  $\text{CO}$ ,  $R$ 's are 2.391 and 2.132 a.u., respectively, taken from ref. 18. Except for  $\text{Be}_2$ ,  $\text{C}_2$ , and  $\text{BF}$ , the distances used in SZ<sup>33</sup> are just the same as those of the present work:  $R = 3.78$ , 2.3475, and 2.385 a.u. for  $\text{Be}_2$ ,  $\text{C}_2$ , and  $\text{BF}$ , respectively.

<sup>b</sup> See ref. 35. Binding energy is given by eV (3.470 eV).

<sup>c</sup> See ref. 33.

<sup>d</sup> The basis set MINI-1 and MINI-3 for H is taken from ref. 36: MINI-1 exponents 4.501800, 0.681444, 0.151398; coefficients 0.070452, 0.407826, 0.647752; and total energy –0.496979 a.u.; MINI-3 exponents 13.013372, 1.962496, 0.444569, 0.121953; coefficients 0.019678, 0.137952, 0.478313, 0.501131; and total energy –0.499278.

<sup>e</sup> See ref. 17.

<sup>f</sup> See ref. 34.

<sup>g</sup> See ref. 18.

**Table XII.** The test on additivity for BSSE<sup>a</sup> (a.u.).

		MINI-1	MIDI-1	MINI-1*	MIDI-1*
C <sub>2</sub>	a.e. (Expect.)	-0.0381	-0.0056	0.0169	0.0257
	a.e. (Calc.)	-0.0385	-0.0064	0.0162	0.0258
N <sub>2</sub>	a.e. (Expect.)	0.0072	0.1075	0.1433	0.1865
	a.e. (Calc.)	0.0068	0.1066	0.1425	0.1868
F <sub>2</sub>	a.e. (Expect.)	-0.0475	-0.0496	-0.0269	-0.0372
	a.e. (Calc.)	-0.0476	-0.0501	-0.0270	-0.0373
Ne <sub>2</sub>	a.e. (Expect.)	-0.0036	-0.0023	-0.0012	-0.0021
	a.e. (Calc.)	-0.0034	-0.0022	-0.0009	-0.0020
BF	a.e. (Expect.)	0.1638	0.1941	0.2203	0.2258
	a.e. (Calc.)	0.1637	0.1938	0.2208	0.2257
CO	a.e. (Expect.)	0.1268	0.2221	0.2446	0.2873
	a.e. (Calc.)	0.1261	0.2214	0.2438	0.2875

<sup>a</sup> a.e. (Expect.) = a.e. (BASE-4) + {a.e. (BASE-2) - a.e. (BASE-4)} + {a.e. (BASE-3) - a.e. (BASE-4)}, where BASE = MINI, MIDI, MINI\*, and MIDI\*.

the extra *p* Gaussian in *p*<sub>1</sub>. For example, the atomization energy difference between MINI-1 and MINI-3 is 0.011 a.u., while that between MINI-1 and MINI-2 is 0.004 a.u. for N<sub>2</sub>. In the second group, the extra *p* Gaussian brings more changes in atomization energies than extra *s* Gaussian. We recall that for these molecules, the orbital energies are strongly affected by the number of expansion terms in *p*<sub>1</sub>. In the third group, extra *p* and *s* Gaussians bring almost the same change in the atomization energies.

It should be noted that for N<sub>2</sub>, the atomization energy (a.e.) differences between MINI-1 and MINI-3 and between MINI-2 and MINI-4 are both ca. 0.011 a.u. and those between MINI-1 and MINI-2 and between MINI-3 and MINI-4 are both ca. 0.004 a.u. These two observations show that the errors caused by the insufficiencies in the expansion terms of *s*<sub>1</sub> and *p*<sub>1</sub> are almost additive. In fact we find

$$\begin{aligned} \text{a.e. (MINI-1)} &\simeq \text{a.e. (MINI-4)} \\ &+ \{\text{a.e. (MINI-2)} - \text{a.e. (MINI-4)}\} \\ &+ \{\text{a.e. (MINI-3)} - \text{a.e. (MINI-4)}\} \end{aligned}$$

The values produced by the right-hand side are given in Table XII, which shows that the additivity of the error stands for other molecules. In conclusion, the largest atomization energy given by MINI-1 among MINI-*i* is due to the accumulation of the errors caused by the insufficiency of the expansion terms in *s*<sub>1</sub> and *p*<sub>1</sub>, although the results

given by all MINI-*i*'s are *sound* in the sense that atomization energies given by MINI-*i* are generally smaller than those given by the extended calculation.

(ii) MIDI-*i*: The split basis sets introduce considerable improvement for all the molecules for which extended calculations give positive atomization energies. They show that it is essential to split the outer shells for describing the molecular environment. The same classifications of the molecules as MINI-*i* hold for MIDI-*i* calculations: C<sub>2</sub> and N<sub>2</sub> make up the first group, BF, F<sub>2</sub>, and Ne<sub>2</sub> the second, and CO the third.

(iii) MINI-1\*: We now face the problem of *s*-type function redundancy in polarization functions mentioned in the previous section. A full discussion is given in the Appendix. The numerical results of molecular calculations are summarized in Table XI. Using the data in Table XI, we find that

$$\begin{aligned} \text{a.e. (MINI-1*)} &\simeq \text{a.e. (MINI-4*)} \\ &+ \{\text{a.e. (MINI-2*)} - \text{a.e. (MINI-4*)}\} \\ &+ \{\text{a.e. (MINI-3*)} - \text{a.e. (MINI-4*)}\} \end{aligned}$$

holds for molecules C<sub>2</sub>, N<sub>2</sub>, F<sub>2</sub>, Ne<sub>2</sub>, BF, and CO (see Table XII). The additivity of errors is thus established even if the polarization function is taken into account; therefore, the rather large atomization energies of MINI-1\* can be attributed to the accumulation of errors.

MINI-4\* gives nearly the same atomization

**Table XIII.** Spectroscopic constants for H<sub>2</sub>.

	a.e. (eV)	$R_e$ (a.u.)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\kappa$ (dyn/cm)
STO-3G	3.48 <sup>a</sup>	1.35 <sup>a</sup>	5400	65.4	0.866E+06
MINI-1	3.49	1.40	5240	61.2	0.815E+06
MINI-3	3.49	1.40	5230	61.4	0.811E+06
MIDI-1	3.48	1.41	4690	60.2	0.652E+06
MIDI-3	3.43	1.42	4680	59.3	0.649E+06
MINI-1*	3.61	1.39	5190	61.8	0.799E+06
MINI-3*	3.60	1.39	5170	62.0	0.794E+06
MIDI-1*	3.57	1.42	4650	59.5	0.642E+06
MIDI-3*	3.54	1.42	4660	59.2	0.646E+06
Extended <sup>b</sup>	3.64	1.39	4561	—	—
Expt.	4.75 <sup>b</sup>	1.40 <sup>b</sup>	4400 <sup>b</sup>	60.8 <sup>c</sup>	0.575E+06 <sup>b</sup>

<sup>a</sup> See ref. 28.<sup>b</sup> See ref. 37.<sup>c</sup> See ref. 27.

energies as MIDI-*i*, except for F<sub>2</sub>. The expansion terms for  $s_1$  and  $p_1$  are supposed to be sufficient and adding the polarization function to the minimal sets has almost the same bearing on the atomization energies.

(iv) MIDI-*i*\*: Except for F<sub>2</sub> and Ne<sub>2</sub> of MIDI-1\* and MIDI-3\*, all the MIDI-*i* calculations give good atomization energies. It is also observed that the role of extra  $p$  Gaussian in the assessments of the atomization energies increases as the nuclear charges in molecule increases.

Table XII shows that the additivity of the error applies in the case of MIDI-*i*\*. To summarize, we

may say that insufficient solidification of the  $p$  shell allows the polarization function to seep into the innermost shell resulting in large atomization energies for the molecules which have large atoms.

#### 4. SPECTROSCOPIC CONSTANTS OF DIATOMIC MOLECULES

In the previous section, we discussed the orbital energies and atomization energies, using the values at a fixed nuclear distance. In this section, the spectroscopic constants, which are calculated by

**Table XIV.** Spectroscopic constants for Li<sub>2</sub>.

	a.e. (eV)	$R_e$ (a.u.)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\kappa$ (dyn/cm)
STO-3G	-0.391	5.18	371	0.646	0.282E+05
MINI-1	-0.093	5.40	330	0.594	0.222E+05
MINI-3	-0.101	5.42	324	0.591	0.215E+05
MIDI-1	-0.098	5.41	311	0.592	0.198E+05
MIDI-3	-0.097	5.41	312	0.593	0.199E+05
MINI-1*	0.102	5.37	347	0.602	0.246E+05
MINI-3*	0.072	5.36	345	0.604	0.243E+05
MIDI-1*	0.096	5.40	333	0.596	0.227E+05
MIDI-3*	0.088	5.40	332	0.596	0.226E+05
Extended <sup>a</sup>	0.17	5.26	336	0.620	0.233E+05
Expt. <sup>a</sup>	1.03	5.05	351	0.673	0.254E+05

<sup>a</sup> See ref. 38.

**Table XV.** Spectroscopic constants for C<sub>2</sub>.

	a.e. (eV)	$R_e$ (a.u.)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\kappa$ (dyn/cm)
STO-3G	-0.956 <sup>a</sup>	2.33 <sup>a</sup>	2220	1.84	0.174E+07
MINI-1	-0.919	2.45	1950	1.67	0.134E+07
MINI-2	-0.882	2.44	1960	1.68	0.137E+07
MINI-3	-1.140	2.45	1930	1.67	0.132E+07
MINI-4	-1.110	2.45	1940	1.68	0.134E+07
MIDI-1	-0.156	2.39	1870	1.76	0.123E+07
MIDI-2	-0.130	2.39	1890	1.76	0.126E+07
MIDI-3	-0.191	2.39	1860	1.76	0.122E+07
MIDI-4	-0.185	2.39	1880	1.75	0.125E+07
MINI-1*	0.465	2.39	2020	1.75	0.145E+07
MINI-2*	0.498	2.39	2020	1.76	0.144E+07
MINI-3*	0.147	2.39	2020	1.75	0.144E+07
MINI-4*	0.163	2.39	2010	1.75	0.143E+07
MIDI-1*	0.705	2.36	1950	1.80	0.134E+07
MIDI-2*	0.642	2.37	1950	1.79	0.134E+07
MIDI-3*	0.693	2.36	1940	1.80	0.134E+07
MIDI-4*	0.632	2.37	1940	1.79	0.134E+07
Extended <sup>b</sup>	(0.789)	2.34	1881	1.83	0.125E+07
Expt. <sup>c</sup>	6.12	2.35	1855	1.82	0.122E+07

<sup>a</sup> See ref. 28.<sup>b</sup> The atomization energy is given only at  $R = 2.3481$  in ref. 17. Spectroscopic constants  $R_e$ ,  $\omega_e$ ,  $B_e$ , and  $\kappa$  are calculated by using the results in ref. 39.<sup>c</sup> See ref. 40.

third-degree polynomials,<sup>27</sup> are discussed; the atomization energies are calculated by using the interpolated total energies. The errors involved in this approach may be estimated to be  $|\Delta D_e| \leq 0.01$  eV,  $\Delta R_e \leq 0.01$  a.u., and  $\Delta \omega_e \leq 2\%$ . As was done in the previous section, the results are always compared with those of extended calculations, because as the size of the basis set becomes larger, the results should approach those of the extended calculations. The molecules presented are H<sub>2</sub>, Li<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, F<sub>2</sub>, CO, and BF. If necessary, the STO-3G calculation is performed. The present calculations are compared with the results of 4-31G if they are available.

### A. H<sub>2</sub> Molecule

The spectroscopic constants derived by various calculations are given in Table XIII. All the present basis sets reproduce the atomization energies and  $R_e$  given by extended calculation. In order to get the proper  $\omega_e$ , the splitting of the outer shell is essential.

The STO-3G gives the poorest values for all the quantities. The calculated  $R_e$  by 4-31G is 1.40 a.u.,<sup>28</sup> which is comparable to those of MINI-1, MINI-3, and MIDI-1.

### B. Li<sub>2</sub> Molecule

The spectroscopic constants for Li<sub>2</sub> are given in Table XIV. The STO-3G gives an atomization energy of -0.4 eV, while MINI-1 and MINI-3 increase the value to -0.1 eV. MINI-1 and MINI-3 give a strange coincidence of  $\omega_e$  to the extended calculation. The quantity  $\omega_e$  calculated by MIDI-1\* and MIDI-3\* is quite close to that calculated by the extended calculation.

Except for  $R_e$  and  $B_e$ , the spectroscopic constants of STO-3G fall behind those of the present basis sets.

### C. C<sub>2</sub> Molecule

The spectroscopic constants for C<sub>2</sub> are given in Table XV. All of the spectroscopic constants are



**Table XVI.** Spectroscopic constants for N<sub>2</sub>.

	a.e. (eV)	$R_e$ (a.u.)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\kappa$ (dyn/cm)
STO-3G	1.65	2.14 <sup>a</sup>	2760	1.87	0.315E+07
MINI-1	0.33	2.14	2620	1.87	0.283E+07
MINI-2	0.22	2.14	2640	1.88	0.286E+07
MINI-3	0.04	2.14	2610	1.87	0.280E+07
MINI-4	-0.07	2.14	2620	1.87	0.283E+07
MIDI-1	2.91	2.05	2660	2.05	0.292E+07
MIDI-2	2.92	2.06	2670	2.02	0.295E+07
MIDI-3	2.86	2.05	2650	2.05	0.291E+07
MIDI-4	2.84	2.06	2670	2.02	0.293E+07
MINI-1*	3.88	2.05	2790	2.04	0.321E+07
MINI-2*	3.64	2.06	2770	2.03	0.316E+07
MINI-3*	3.49	2.05	2780	2.04	0.319E+07
MINI-4*	3.23	2.06	2760	2.03	0.315E+07
MIDI-1*	5.12	2.03	2730	2.08	0.308E+07
MIDI-2*	4.94	2.04	2750	2.07	0.311E+07
MIDI-3*	5.09	2.03	2730	2.08	0.307E+07
MIDI-4*	4.92	2.04	2740	2.07	0.311E+07
Extended <sup>b</sup>	5.27	2.01	2730	2.12	0.307E+07
Expt. <sup>b</sup>	9.90	2.07	2358	2.00	0.229E+07

<sup>a</sup> See ref. 41.<sup>b</sup> See ref. 42.**Table XVII.** Spectroscopic constants for F<sub>2</sub>.

	a.e. (eV)	$R_e$ (a.u.)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\kappa$ (dyn/cm)
STO-3G	0.20	2.49 <sup>a</sup>	1690	1.020	0.160E+07
MINI-1	-1.29	2.67	1340	0.889	0.100E+07
MINI-2	-2.00	2.70	1270	0.872	0.908E+06
MINI-3	-1.40	2.68	1340	0.884	0.100E+07
MINI-4	-2.10	2.70	1270	0.867	0.904E+06
MIDI-1	-1.36	2.67	1250	0.888	0.872E+06
MIDI-2	-2.00	2.67	1140	0.888	0.722E+06
MIDI-3	-1.39	2.67	1250	0.886	0.873E+06
MIDI-4	-2.04	2.68	1140	0.885	0.722E+06
MINI-1*	-0.66	2.58	1290	0.950	0.927E+06
MINI-2*	-1.22	2.60	1300	0.939	0.953E+06
MINI-3*	-0.95	2.60	1270	0.940	0.909E+06
MINI-4*	-1.51	2.61	1290	0.930	0.932E+06
MIDI-1*	-0.92	2.56	1150	0.970	0.734E+06
MIDI-2*	-1.34	2.52	1130	0.998	0.719E+06
MIDI-3*	-0.93	2.56	1150	0.966	0.734E+06
MIDI-4*	-1.35	2.53	1130	0.994	0.717E+06
Extended <sup>b</sup>	-1.37	2.50	1257	1.003	0.884E+06
Expt. <sup>c</sup>	1.68	2.68	932	0.890	0.486E+06

<sup>a</sup> See ref. 41.<sup>b</sup> See refs. 37 and 43.<sup>c</sup> See ref. 44.

**Table XVIII.** Spectroscopic constants for BF.

	a.e. (eV)	$R_e$ (a.u.)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\kappa$ (dyn/cm)
STO-3G	4.34	2.36	1650	1.60	0.108E+07
MINI-1	4.51	2.47	1540	1.44	0.966E+06
MINI-2	4.10	2.47	1460	1.43	0.870E+06
MINI-3	4.29	2.48	1520	1.42	0.940E+06
MINI-4	3.88	2.48	1440	1.42	0.847E+06
MIDI-1	5.33	2.48	1490	1.43	0.899E+06
MIDI-2	4.85	2.51	1320	1.39	0.708E+06
MIDI-3	5.26	2.48	1480	1.42	0.890E+06
MIDI-4	4.76	2.51	1310	1.39	0.696E+06
MINI-1*	6.01	2.41	1610	1.50	0.105E+07
MINI-2*	5.67	2.40	1560	1.52	0.984E+06
MINI-3*	5.53	2.42	1580	1.49	0.102E+07
MINI-4*	5.20	2.41	1530	1.50	0.952E+06
MIDI-1*	6.14	2.41	1510	1.50	0.924E+06
MIDI-2*	5.92	2.38	1470	1.54	0.871E+06
MIDI-3*	6.12	2.41	1500	1.50	0.918E+06
MIDI-4*	5.89	2.39	1460	1.53	0.863E+06
Extended <sup>a</sup>	6.23	2.36	1500	1.57	0.916E+06
Expt. <sup>b</sup>	8.58 ± 0.5	2.39	1402	1.51	0.807E+06

<sup>a</sup> The results are obtained by using the energies given in ref. 18.

<sup>b</sup> See ref. 45.

considerably improved by the MIDI-*i* calculations. Further improvement is achieved by MIDI-*i*\*, except for  $\omega_e$ .

The distance  $R_e$  calculated by STO-3G agrees with that of extended calculation. The atomization energy calculated by 4-31G at  $R_e$  of STO-3G is -0.189 eV,\* which is nearly the same as those of MIDI-3 and MIDI-4.

#### D. N<sub>2</sub> Molecule

The spectroscopic constants for N<sub>2</sub> are given in Table XVI. The MIDI-*i* calculations improve the spectroscopic constants to a great extent compared with the MINI-*i* calculations. Further improvements are accomplished by adding the polarization functions: the results given by MIDI-*i*\* (*i* = 1, 2, 3, 4) are satisfactory.

We note that the spectroscopic constants by MINI-4\* are close to those of MIDI-*i* except  $\omega_e$  and  $\kappa$ .

The STO-3G yields remarkably large atomiza-

tion energies among the minimal-type basis sets. This may be a result of the extreme energy decreases in  $1\sigma_g$  and  $1\sigma_u$  which will be shown in the case of F<sub>2</sub>. The equilibrium distance  $R_e$  by 4-31G is 2.05 a.u.,<sup>29</sup> which is the same as those of MIDI-1 and MIDI-3.

#### E. F<sub>2</sub> Molecule

The spectroscopic constants for F<sub>2</sub> are given in Table XVII. The similarities between the BASE-*i* and BASE-*i* + 2 (BASE = MINI, MIDI, and MIDI\*) are observed in almost all the quantities. Rather large atomization energies by MINI-*i*\* (*i* = 1, 3) and MIDI-*i*\* (*i* = 1, 3) are due to accumulation of errors.

The STO-3G gives a molecular distance in good agreement with that of the extended basis set but yields a positive binding energy. The latter result might be the result of the large energy decrease in the  $1\sigma_g$  and  $1\sigma_u$  orbital energies compared with the atomic  $1s$  orbital energy: for example, at  $R = 2.68$  a.u., the difference between  $\epsilon_{1\sigma_{g,u}}$  and  $\epsilon_{1s}$  by STO-3G is around -0.111 a.u. while the quantities are from -0.036 to -0.050 a.u. for the other minimal sets. Adding a  $3d$  orbital, whose exponent is de-

\* Using their total energy for C<sub>2</sub> (-75.26497) and the result for C in Table I, we have recalculated the atomization energy; original value was -0.241 eV.

**Table XIX.** Spectroscopic constants for CO.

	a.e. (eV)	$R_e$ (a.u.)	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\kappa$ (dyn/cm)
STO-3G	5.24	2.17 <sup>a</sup>	2500	1.87	0.254E+07
MINI-1	3.74	2.26	2130	1.72	0.184E+07
MINI-2	3.44	2.26	2090	1.72	0.177E+07
MINI-3	3.49	2.26	2110	1.71	0.179E+07
MINI-4	3.18	2.27	2060	1.71	0.171E+07
MIDI-1	6.02	2.13	2330	1.93	0.219E+07
MIDI-2	5.87	2.14	2310	1.92	0.216E+07
MIDI-3	5.95	2.14	2320	1.92	0.217E+07
MIDI-4	5.77	2.14	2310	1.92	0.215E+07
MINI-1*	6.65	2.16	2390	1.88	0.231E+07
MINI-2*	6.45	2.16	2370	1.88	0.227E+07
MINI-3*	6.22	2.16	2380	1.87	0.228E+07
MINI-4*	6.01	2.16	2360	1.88	0.224E+07
MIDI-1*	7.85	2.10	2460	1.99	0.244E+07
MIDI-2*	7.76	2.10	2460	1.99	0.244E+07
MIDI-3*	7.81	2.10	2450	1.99	0.243E+07
MIDI-4*	7.74	2.10	2460	1.99	0.244E+07
Extended <sup>b</sup>	7.97	2.08	2480	2.02	0.248E+07
Expt. <sup>c</sup>	11.24	2.13	2170	1.93	0.190E+07

<sup>a</sup> See ref. 29.<sup>b</sup> The results are obtained by using the energies given in ref. 18.<sup>c</sup> See ref. 45.

terminated by eq. (5), to STO-3G, we find the atomization energy of 1.06 eV at  $R_e$  of STO-3G. Superficially, this value is in good agreement with the experimental value of 1.68 eV, while, as is well known, the near Hartree-Fock calculation cannot even produce the binding energy. One might regard or exploit the situation as a blessing for the advantage of STO-3G, but it must be clearly understood that the good atomization is a result of errors.

## F. BF Molecule

The spectroscopic constants for BF are given in Table XVIII. They behave in the same manner as those for F<sub>2</sub>, along with the change of basis sets. The constants by MIDI- $i^*$  ( $i = 1, 2, 3, 4$ ) are in accord with those by the extended calculation. The  $R_e$  of STO-3G coincides with that of the extended calculation.

## G. CO Molecule

The spectroscopic constants for CO are given in Table XIX. They are improved in the order of

MINI-1, MIDI-1, and MIDI-1\* and so on. The results of MIDI- $i^*$  ( $i = 1, 2, 3, 4$ ) are satisfactory.

**Table XX.** Total energies for C<sub>2</sub>H<sub>2</sub>,<sup>a</sup> C<sub>2</sub>H<sub>4</sub>,<sup>b</sup> and C<sub>3</sub>H<sub>6</sub><sup>c</sup> (a.u.).

	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>
STO-3G	-75.85204	-77.07090	-115.66553
MINI-1	-76.28042	-77.48238	-116.24359
MIDI-1	-76.36276	-77.56562	-116.34056
MIDI-2	-76.39929	-77.60615	-116.41096
MIDI-3	-76.66391	-77.86766	-116.79087
MIDI-4	-76.70194	-77.91057	-116.86393
Extended	-76.85397 <sup>d</sup>	-78.0623 <sup>e</sup>	-117.0099 <sup>f</sup>

<sup>a</sup> Molecular geometries for C<sub>2</sub>H<sub>2</sub> are  $r_{C-C} = 2.2810$  a.u. and  $r_{C-H} = 2.0020$  a.u. which are given in ref. 18.<sup>b</sup> Molecular geometries for C<sub>2</sub>H<sub>4</sub> are  $r_{C-C} = 2.5510$  a.u.,  $r_{C-H} = 2.0336$  a.u., and  $\angle HCH = 117^\circ$  which are adapted by Fischer-Hjalmar and Siegbahn.<sup>21</sup><sup>c</sup> Molecular geometries for C<sub>3</sub>H<sub>6</sub> are those which are adapted by Bash, Robins, and Kuebler.<sup>46</sup><sup>d</sup> See ref. 18.<sup>e</sup> See ref. 21.<sup>f</sup> See ref. 46. The polarization functions are not included in this calculation.

**Table XXI.** Orbital energies and ionization potentials for C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>6</sub>.

	STO-3G	MINI-1	MIDI-1	MIDI-2	MIDI-3	MIDI-4	Extended	Expt.
<b>C<sub>2</sub>H<sub>2</sub> molecule</b>								
2σ <sub>g</sub>	25.90 eV	28.67	28.17	28.21	28.28	28.28	28.02 <sup>a</sup>	23.4 <sup>b</sup>
2σ <sub>u</sub>	19.28	21.09	20.62	20.73	20.69	20.78	20.95 <sup>a</sup>	18.6 <sup>b</sup>
3σ <sub>g</sub>	16.56	18.65	18.36	18.54	18.38	18.55	18.58 <sup>a</sup>	16.7 <sup>b</sup>
1π <sub>u</sub>	9.45	12.05	10.98	11.19	11.01	11.19	11.17 <sup>a</sup>	11.4 <sup>b</sup>
<b>C<sub>2</sub>H<sub>4</sub> molecule</b>								
1b <sub>2u</sub>	16.40 eV	17.98	17.43	17.56	17.47	17.58	17.59 <sup>b</sup>	15.9 <sup>b</sup>
3a <sub>g</sub>	14.42	16.27	15.78	15.98	15.82	15.98	16.01 <sup>b</sup>	14.8 <sup>b</sup>
1b <sub>3g</sub>	12.71	14.23	13.69	13.82	13.74	13.85	14.01 <sup>b</sup>	12.4 <sup>b</sup>
1b <sub>3u</sub>	8.71	11.13	10.07	10.14	10.11	10.14	10.13 <sup>b</sup>	10.5 <sup>b</sup>
<b>C<sub>3</sub>H<sub>6</sub> molecule</b>								
1a <sub>2</sub>	17.35 eV	19.02	18.35	18.30	18.38	18.31	18.29 <sup>c</sup>	16.5 <sup>c</sup>
3a <sub>1</sub>	15.86	17.54	16.90	17.00	16.96	17.01	16.95 <sup>c</sup>	15.7 <sup>c</sup>
1e''	13.04	14.56	13.91	13.91	13.98	13.96	13.89 <sup>c</sup>	13.2 <sup>c</sup>
3e'	10.36	12.48	11.45	11.45	11.53	11.47	11.40 <sup>c</sup>	10.5 <sup>c</sup>

<sup>a</sup> See ref. 18.<sup>b</sup> See ref. 21.<sup>c</sup> See ref. 46.

The distance  $R_e$  calculated by 4-31G is 2.13 a.u.,<sup>29</sup> which is the same value given by MIDI-1.

## 5. SOME APPLICATIONS TO ORGANIC MOLECULES

We have found that MIDI-*i* are effective for calculating the homo- and heterodiatomics. In this section, MINI-1 and MIDI-*i* (*i* = 1–4) are applied to the calculations of organic molecules C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>6</sub>. The calculation which includes the polarization function is not performed because such a calculation is beyond the present purpose of investigating the effectiveness of the basis sets.

The total energies are given in Table XX. They

**Table XXII.** C—C bond distance and atomization energies for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>.

	a.e. (eV)		C—C bond (a.u.)	
	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>
STO-3G	11.1	17.3	2.21 <sup>a</sup>	2.47 <sup>a</sup>
MINI-1	10.4	16.0	2.28	2.54
MIDI-1	11.9	17.6	2.24	2.49
MIDI-2	12.0	17.9	2.26	2.50
MIDI-3	11.6	17.2	2.24	2.49
MIDI-4	11.8	17.6	2.26	2.50
Expt.	—	—	2.27	2.51

<sup>a</sup> See ref. 41.

are not far from the extended calculations; the differences are around 0.15 a.u.

The orbital energies of the four highest orbitals for these molecules are given and compared with the experimental ionization potentials in Table XXI.

The orbital energies of MIDI-*i* always agree with those of the large-scale calculations. They give larger ionization potentials than experiments except for the first ionization potentials of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> for which the MIDI-*i* and the extended calculations yield slightly smaller values than experiments. The STO-3G set produces good agreement with experiments for the higher ionization potentials. The reason for this could be traced back to the shallow atomic orbital energies. The  $\Delta E(\text{SCF})$  method, where the ionization potential is calculated by the independent calculations for the ionic and neutral molecules, predicts smaller ionization potentials than the method of Koopman's theorem. For C<sub>2</sub>H<sub>4</sub>, the ionization potentials by the  $\Delta E(\text{SCF})$  method are reported to be 8.91, 13.31, 14.47, and 16.76 eV<sup>21</sup> for the first four states. These values are smaller than those of MIDI-*i* and the extended sets given by Koopman's theorem, while those of STO-3G are even smaller than those given by the  $\Delta E(\text{SCF})$  method, except for the third one.

In Table XXII, atomization energies and C—C

**Table XXIII.** Total energies and orbital energies given by the set corrected by additional 3s function.

	B	C	N	O	F	Ne
<b>Total energies</b>						
MINI-1'	-24.37708	-37.45794	-54.06956	-74.34845	-98.78930	-127.73360
MINI-2'	-24.38145	-37.47284	-54.10324	-74.41422	-98.90094	-127.90724
MINI-3'	-24.48670	-37.61648	-54.28516	-74.62971	-99.14451	-128.17309
MINI-4'	-24.49106	-37.63134	-54.31880	-74.69538	-99.25608	-128.34658
MIDI-1'	-24.38906	-37.47336	-54.09274	-74.37615	-98.82616	-127.77948
MIDI-2'	-24.39347	-37.48833	-54.12657	-74.44215	-98.93798	-127.95333
MIDI-3'	-24.48916	-37.62008	-54.29020	-74.63629	-99.15291	-128.18365
MIDI-4'	-24.49353	-37.63494	-54.32384	-74.70201	-99.26449	-128.35712
<b>1s orbital energies</b>						
MINI-1'	-7.64107	-11.24369	-15.51507	-20.51756	-26.18418	-32.52073
MINI-2'	7.63915	-11.24113	-15.51030	-20.51047	-26.17917	-32.51557
MINI-3'	-7.68216	-11.30610	-15.60215	-20.63266	-26.33323	-32.70851
MINI-4'	-7.68039	-11.30327	-15.59737	-20.62632	-26.32756	-32.70243
MIDI-1'	-7.65714	-11.26202	-15.53886	-20.54367	-26.21636	-32.55957
MIDI-2'	-7.65523	-11.25935	-15.53408	-20.53657	-26.21104	-32.55399
MIDI-3'	-7.68896	-11.31414	-15.61200	-20.64342	-26.34575	-32.72310
MIDI-4'	-7.68721	-11.31134	-15.60729	-20.63738	-26.34020	-32.71708
<b>2s orbital energies</b>						
MINI-1'	-0.49243	-0.69999	-0.93576	-1.22795	-1.54645	-1.89379
MINI-2'	-0.49275	-0.70184	-0.93919	-1.23420	-1.55799	-1.91054
MINI-3'	-0.49340	-0.70185	-0.93830	-1.23140	-1.55143	-1.90038
MINI-4'	-0.49372	-0.70352	-0.94159	-1.23782	-1.56266	-1.91666
MIDI-1'	-0.49158	-0.69871	-0.93379	-1.22560	-1.54361	-1.89063
MIDI-2'	-0.49180	-0.70037	-0.93701	-1.23158	-1.55477	-1.90691
MIDI-3'	-0.49328	-0.70158	-0.93789	-1.23078	-1.55071	-1.89953
MIDI-4'	-0.49358	-0.70320	-0.94114	-1.23717	-1.56185	-1.91569
<b>2p orbital energies</b>						
MINI-1'	-0.30485	-0.42339	-0.55070	-0.60347	-0.68654	-0.79029
MINI-2'	-0.30924	-0.43179	-0.56427	-0.62540	-0.71956	-0.83527
MINI-3'	-0.30400	-0.42215	-0.54913	-0.60131	-0.68433	-0.78786
MINI-4'	-0.30850	-0.43055	-0.56276	-0.62347	-0.71722	-0.83264
MIDI-1'	-0.30536	-0.42365	-0.55066	-0.60308	-0.68588	-0.78958
MIDI-2'	-0.30987	-0.43201	-0.56412	-0.62482	-0.71858	-0.83415
MIDI-2'	-0.30444	-0.42258	-0.54962	-0.60167	-0.68468	-0.78821
MIDI-2'	-0.30895	-0.43101	-0.56323	-0.62384	-0.71753	-0.83291

bond distances are listed for  $C_2H_2$  and  $C_2H_4$ . The C—H bond distances are fixed (see footnote a and b to Table XX). The results of the extended calculations are not available. The estimated C—C bond distances by MIDI-*i* are in accord with experiments, especially for MIDI-2 and MIDI-4.

The STO-3G set produces shorter C—C bond distances. Those calculated by 4-31G<sup>29</sup> are 2.25 and 2.49 a.u. for  $C_2H_2$  and  $C_2H_4$ , respectively, which are almost the same as those by MIDI-*i* (*i* = 1, 2, 3, and 4).

## 6. CONCLUDING REMARKS

In the two previous articles<sup>11,12</sup> of the present series, we had a well-defined objective. We started with the observation that for the first transition metal elements the single-zeta (minimum) STO basis set is obviously inadequate, and we attempted and succeeded to prepare a viable, as a matter of fact far better, alternative to the minimum STO basis set in the form of minimum contracted GTO.

**Table XXIV.** Comparison of exponents of polarization function.

	OVLP	OPTM
H	0.68	0.876
Li	0.07	0.139
Be	0.16	0.264
C	0.61	0.410
N	0.87	0.546
F	1.50	0.938
Ne	1.89	1.146

In this article we venture into the territory where the STO-3G basis set claims an immense popularity which is certainly not without reason. Indeed, the STO-3G basis set produces various molecular quantities in good agreement with experiment. Here, however, we confront unavoidably the problem of empiricism in the so-called *ab initio* molecular calculation when we are obliged to use small-sized basis sets.

The parametrization of the STO-3G basis sets can be characterized as a statistical fine-tuning so that the computed molecular quantities exhibit a wide range of good agreement with *experiment*. Basically there is nothing wrong with a healthy empiricism in theoretical science. It is often useful, revealing, and even indispensable. However, in the case of *ab initio* MO-SCF calculations, we must be well aware of the existence of fairly well-defined limit of attainable accuracy which is set by the near Hartree-Fock calculation.

The F<sub>2</sub> molecule provides a good case in point. The near Hartree-Fock calculation gives 2.50 a.u. as the equilibrium internuclear distance  $R_e$ , which is reasonably close to the experimental value of

2.68 a.u., but the atomization energy is calculated to be -1.37 eV, which means no binding, whereas the experimental value is +1.68 eV. Now, the STO-3G basis set gives 2.49 a.u. for  $R_e$  and +0.20 eV for the atomization energy. Furthermore, if a 3d function is added to STO-3G as a polarization function, the computed atomization becomes +1.06 eV, in close agreement with experiment. Should we regard this result as a blessing or a curse?

In the present work we have attempted to identify the sources of errors so that we can eliminate the empirical nature of small basis sets as much as possible by using results of extended basis set calculations as the benchmark. We summarize some important conclusions that we have reached during the course of the present work.

(1) Primarily because of their compactness, MINI-1 and especially MIDI-1 are recommended for use in a wide range of molecular calculations. According to the findings given above, we can expect that the MIDI-1 basis set, which could be denoted as 3-21G in Pople's notation, provides calculated results of similar quality to those by Pople's 4-31G. In a forthcoming article,<sup>30</sup> we shall show that the MIDI-1 sets give even slightly better spectroscopic constants than 4-31G for molecules containing third-row atoms as well as second-row atoms.

(2) It would be recommended to use the split basis sets MIDI-*i* rather than minimal sets plus polarization functions MINI-*i*\*.

(3) The onset of the BSSE can be prevented mainly by increasing the number of expansion terms of  $p_1$ . Our numerical results show that MIDI-1\*, -3\* and MIDI-2\*, -4\* may be judged safe

**Table XXV.** Comparison of atomization energies.

	H <sub>2</sub>	Li <sub>2</sub>	Be <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
MINI-1* (OVLP)	0.1326	0.0029	-0.0557	0.0162	0.1425	-0.0270	-0.0009
MINI-2* (OVLP)	—	—	—	0.0175	0.1336	-0.0469	-0.0036
MIDI-1* (OVLP)	0.1312	0.0025	-0.0452	0.0258	0.1868	-0.0373	-0.0020
MIDI-2* (OVLP)	—	—	—	0.0234	0.1807	-0.0546	-0.0064
MINI-1* (OPTM)	0.1328	0.0040	-0.0525	-0.0110	0.1002	-0.0962	-0.0881
MINI-2* (OPTM)	—	—	—	-0.0098	0.0911	-0.1163	-0.0912
MIDI-1* (OPTM)	0.1314	0.0040	-0.0354	0.0273	0.1895	-0.0345	0.0012
MIDI-2* (OPTM)	—	—	—	0.0250	0.1835	-0.0517	-0.0031
Extended	0.1336 <sup>a</sup>	0.0061 <sup>a</sup>	-0.0285 <sup>a</sup>	0.0290 <sup>a</sup>	0.1910 <sup>a</sup>	-0.0504 <sup>a</sup>	-0.0085 <sup>b</sup>

<sup>a</sup> See ref. 17.

<sup>b</sup> See ref. 34.

to use for molecules consisting of atoms with  $Z \leq 8$  (MIDI-1\*, -3\*) and  $Z \leq 9$  (MIDI-2\*, -4\*). These basis sets produce consistently reliable calculational values that are close to values given by far more expensive basis sets.

Figure 1(c) shows that the error of  $2p$  by MINI-1 increases as the nuclear charge increases. This indicates that in order to balance the basis sets, one needs to combine the different basis sets such as MINI-1 and MINI-2 for molecules containing different atoms.

We have discussed the atomization energy to a considerable extent and we have used the adjective "sound" for atomization energies several times. When we calculate relative energy differences on a molecular energy surface (curve) by the MO-SCF method, we may sometimes obtain a good agreement with experiment because of a fortuitous cancellation of electron correlation energies that actually exist but cannot be accounted for within the framework of the SCF method. However, it is quite a different matter if a good agreement with experiment is brought about by BSSE, because it is an artifact due to inadequacies of small basis sets. From a semiempirical point of view, we may exploit the situation to our advantage, but we do not share such a view in the present work.

The calculations for molecules were performed by the modified version<sup>31</sup> of MOLECULE originally developed by Almlöf.<sup>32</sup>

## APPENDIX

### The Corrected Atomic Energies Used with Six-Membered $d$ -Type Gaussian Functions

In many molecular SCF and CI calculation programs including the MOLECULE program,<sup>31,32</sup> six-membered  $d$ -type Gaussian functions

$$(x^2, y^2, z^2, xy, yz, zx)e^{-\gamma r^2}$$

are used. They contain one  $3s$ -type function

$$(x^2 + y^2 + z^2)e^{-\gamma r^2} = r^2e^{-\gamma r^2} \quad (\text{A1})$$

in addition to five genuine  $d$ -type functions. As a result, whenever we use  $d$ -type functions in such molecular programs, we "inadvertently" add a new  $3s$ -type Gaussian function to the atomic site on which six-membered  $d$ -type functions are placed. Therefore, in order to be consistent in the computation of atomization energies, the reference atomic energies should be recalculated by taking

into account these additional  $3s$  Gaussian functions, because the effects are quite sizable if the original atomic orbital bases are rather small and not reasonably saturated.

The corrected atomic total energies and orbital energies are given in Table XXIII, which are computed by adding the term in (A1) with the value of  $\gamma$  taken from Table V. Comparison of Tables I and XXIII shows that the correction produces considerable effects for MINI- $i$  and MIDI- $i$  ( $i = 1, 2$ ) amounting to 0.004–0.015 a.u. If we calculate the atomization energy of  $F_2$  molecule by MIDI-2\*, we obtain  $-0.56$  eV *without* the correction,  $-1.34$  eV *with* the correction, the difference reaching 0.8 eV (18 kcal/mole). For  $i = 3, 4$  the correction produces almost negligible effects.

We shall now examine the problem of how to determine orbital exponents of polarization functions in light of the preceding discussions.

Using MINI-1 plus polarization functions, we made SCF calculations on homonuclear diatomic molecules and determined the exponents of the polarization functions which give the optimum energy. The resulting exponents are given in Table XXIV together with those from Table V. Adding these polarization functions to MINI-2, MIDI-1, and MIDI-2, we again performed SCF calculations on the diatomics. The results are given in Table XXV. The symbol OPTM in Tables XXIV and XXV indicates that the polarization functions are determined by the method given above, while OVLP indicates optimization by maximizing the overlap as given by eq. (5).

Table XXV shows that MINI-1\* (OPTM) gives smaller atomization energies than MINI-1\* (OVLP). At first glance, the result is curious but it is justified because the decrease in the "molecular" total energy actually happens in a form of decreasing the "atomic portion" of the molecular total energy if the original basis set is as small as MINI-1. It is thus dangerous to optimize exponents of the polarization function in this way if the atomic functions are not sufficiently large.

Comparing the results in Table XXIV, one may also observe that the atomization energies given by MIDI-1\* and MIDI-2\* are almost independent of changes in the exponent of the polarization function. It is well known that the atomization energy varies very slowly with changes in polarization functions, when the original set is sufficiently large. In this respect, the characteristics of MIDI-1 and MIDI-2 are satisfactory as basis sets.

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