A Systematic Preparation of New Contracted Gaussian-Type Orbital Sets. V. From Na Through Ca

Yoshiko Sakai,* Hiroshi Tatewaki,† and Sigeru Huzinaga

The Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada
Received 26 June 1980; accepted 12 September 1980

Minimal compact contracted Gaussian basis sets are constructed for the atoms from Na to Ca. They give satisfactory valence shell orbital energies, although they are minimal-type basis sets. Split-type basis sets are also derived from the minimal Gaussian basis sets in order to enhance the flexibility of the basis sets for molecular calculations.

I. INTRODUCTION

Compact contracted Gaussian-type basis sets were previously presented for the second-row atoms (Li–Ne)[1] and the first-transition metal atoms (Sc–Zn).[2] In this article, the coverage is extended to the atoms from Na to Ca in their ground states.

Pople's group published STO-kG (k = 2, 3, 4, 5, or 6) for the third-row atoms (Na–Ar)[3] and 44-31G for P, S, and Cl.[4] The STO-kG sets have been determined so as to simulate the single-zeta STO (SZ) basis sets. Unfortunately, the SZ functions determined by optimizing atomic total energies give very poor valence shell orbital energies. Therefore, even if a number of primitive Gaussian functions are used to simulate the SZ functions, the STO-kG sets may not describe the valence region of atoms properly. The 44-31G sets have been determined by optimizing atomic total energies without making any use of SZ (STO) as reference. However, a constraint in which the same exponent is used for the s- and the p-type function, such as $\zeta_{3s} = \zeta_{3p}$, is imposed on both STO-kG and 44-31G for economical reasons. Three groups of minimal basis sets have been constructed and named MINI-1, MINI-3, and MINI-4. More descriptive shorthand

notations are (33../33..), (43../33..), and (43../43..) for i = 1, 3, and 4 in MINI-i, respectively. The detail of the terminology is given in ref. 1. Orbital exponents and contraction coefficients were determined through optimizing atomic total energies, but the process of contraction and decontraction was conducted in such a way that overspending too many primitive Gaussian functions in the inner-core region of the atom was avoided and good valence shell orbital energies were obtained, which are very close to those of double-zeta (DZ) STOs. The total atomic energies given by MINI-3 are lower than those of SZ for almost all the atoms treated here.

In order to enhance the flexibility of basis sets for molecular calculations, split basis sets— semi-MIDI-i (SMIDI-i) and MIDI-i (i = 1, 3, and 4)—are derived from MINI-i sets. In these basis sets, valence shell orbitals of parent MINI-i sets are split into two parts, one part consisting of one GTO and the other consisting of (n-1) GTOs, n being the number of primitive GTOs before splitting. We split both s and p valence orbitals in MIDI-i sets, while only the p valence orbital is split in the SMIDI-i sets.* These split basis sets

---

* Permanent address: College of General Education, Kyushu University, Fukuoka, Japan.
† Permanent address: The Research Institute for Catalysis, Hokkaido University, Sapporo, Japan.

---

* Radial parts of the valence orbitals for the third-row atoms are given as $R_{3s} = C_{3s,1}s_1 + C_{3s,2}s_2 + C_{3s,3}s_3$ and $R_{3p} = C_{3p,1}p_1 + C_{3p,2}p_2$. s_3 and p_2, which are the main components of $3s$ and $3p$ orbitals, are split. See Sec. II for details.

Table I. Shorthand description for various kinds of contracted Gaussian basis sets.[a]

Basis Set	Na, Mg	Al–Ar	K, Ca
MINI-1	(333/3)	(333/33)	(3333/33)
MINI-3	(433/3)	(433/33)	(4333/33)
MINI-4	(433/4)	(433/43)	(4333/43)
SMIDI-1	---	(333/321)	---
SMIDI-3	---	(433/321)	---
SMIDI-4	---	(433/421)	---
MIDI-1	(3321/3)	(3321/321)	(33321/33)
MIDI-3	(4321/3)	(4321/321)	(43321/33)
MIDI-4	(4321/4)	(4321/421)	(43321/43)

[a] SMIDI-i (i = 1, 3, and 4) cannot be defined for Na, Mg, K, and Ca because they have no p-type valence orbital. See text for details.

give only slightly lower atomic total energies but are capable of describing molecular environments much more effectively than the parent nonsplit basis sets, as will be shown in a future article.

II. ATOMIC WAVEFUNCTIONS

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

In the minimal basis sets, the radial functions of the atomic orbitals are expressed as

$$R_{ns}(r) = \sum_{i=1}^{N} C_{ns,i} s_i(r) \qquad (1)$$

N = 3 for Na to Ar, and N = 4 for K and Ca, and

$$R_{np}(r) = \sum_{i=1}^{N} C_{np,i} p_i(r) \qquad (2)$$

N = 1 for Na and Mg, and N = 2 for Al to Ca, where n is the principal quantum number and the functions $\{s_i(r)\}$ and $\{p_i(r)\}$ can be chosen arbitrarily. In the present work, we use K primitive Gaussian functions to construct one $s_i(r)$ or $p_i(r)$ function, which can be written as

$$s_i(r) = \sum_{k=1}^{K} d_{s_i,k} g_{s_i}(\alpha_{s_i,k}, r) \qquad (3)$$

and

$$p_i(r) = \sum_{k=1}^{K} d_{p_i,k} g_{p_i}(\alpha_{p_i,k}, r) \qquad (4)$$

where g_{s_i} and g_{p_i} are normalized $1s$-type and $2p$-type functions, respectively. Three GTOs are used in MINI-1 for both s_i (i = 1, 2, 3, 4) and p_i (i = 1, 2). The basis sets may be expressed as (333/3) for Na and Mg, (333/33) for Al to Ar, and (3333/33) for K and Ca. Four primitive GTOs are used for s_1 in MINI-3, and for s_1 and p_1 in MINI-4. Table I gives a summary of their shorthand descriptions for quick reference.

The expansion coefficients and the exponents of GTOs have been determined by the same method reported elsewhere.[2] Optimization of parameters was terminated when the Δ value defined below became less than 5×10^{-7}:

$$\Delta = [E^{total}(n) - E^{total}(n - 1)]/E^{total}(n) \qquad (5)$$

where $E^{total}(n - 1)$ and $E^{total}(n)$ are the total energies of two consecutive optimization rounds, all contracted functions, s_i's and p_i's, being optimized for each round. The MINI-1, MINI-3, and MINI-4 basis sets thus obtained are shown in Tables II–IV.

B. MIDI-i and SMIDI-i (i = 1, 3, and 4)

The MIDI-i and SMIDI-i basis sets were derived from MINI-i sets, and their shorthand descriptive notations are given in Table I. Reoptimization of parameters has been consciously avoided because it was found that if exponents of the split functions were varied, the inner part of the split function was drawn toward the inside in order to lower the atomic total energy at the expense of the deterioration of the valence region description. This tendency goes obviously against our original objective of constructing compact basis sets effective for describing molecular electronic states. Therefore, the MIDI-i and the SMIDI-i sets have been derived merely by partitioning the s_3 (or s_4 for K and Ca) and/or the p_2 functions in the MINI-i sets into two parts without changing exponents and coefficients given in Tables II–IV.

Table II. Exponents and expansion coefficients for MINI-1.

	Na Expn.	Na Coef.	Mg Expn.	Mg Coef.	Al Expn.	Al Coef.	Si Expn.	Si Coef.
s_1	542.76053	0.06841	650.64367	0.06803	777.16054	0.06690	908.99529	0.06641
	81.95947	0.39209	98.37078	0.39074	117.23701	0.38773	137.15292	0.38614
	17.72377	0.66608	21.32249	0.66727	25.37912	0.67072	29.72061	0.67231
s_2	23.28042	-0.08380	27.97738	-0.08672	33.29314	-0.08913	39.03949	-0.09118
	1.86834	0.58279	2.32652	0.58570	2.82157	0.59416	3.36039	0.60403
	0.62325	0.49247	0.81808	0.48650	1.03275	0.47574	1.26523	0.46444
s_3	0.50673	-0.11576	0.91134	-0.12765	1.34771	-0.15156	1.81658	-0.16879
	0.05351	0.69585	0.09940	0.65077	0.15977	0.66605	0.22492	0.67829
	0.02080	0.38104	0.03623	0.43627	0.05832	0.43093	0.08199	0.42579
p_1	17.83636	0.12571	23.21663	0.12146	29.98078	0.11493	37.35735	0.11047
	3.79569	0.48046	5.00222	0.47929	6.54688	0.47028	8.21894	0.46552
	0.87751	0.60228	1.20465	0.59894	1.63911	0.60477	2.10672	0.60787
p_2					2.91293	-0.00961	4.62206	-0.01451
					0.24083	0.38496	0.33406	0.44642
					0.06916	0.71208	0.09689	0.65610

	P Expn.	P Coef.	S Expn.	S Coef.	Cl Expn.	Cl Coef.	Ar Expn.	Ar Coef.
s_1	1054.02086	0.06580	1197.75297	0.06596	1358.82774	0.06569	1533.07396	0.06531
	158.93176	0.38435	181.09550	0.38426	205.55039	0.38328	231.87032	0.38211
	34.44277	0.67423	39.37593	0.67389	44.73923	0.67481	50.48390	0.67603
s_2	45.30474	-0.09289	51.98935	-0.09445	59.22575	-0.09574	66.95512	-0.09687
	3.93872	0.61524	4.56684	0.62604	5.22992	0.63806	5.93818	0.64902
	1.51423	0.45221	1.78167	0.44084	2.06114	0.42840	2.35734	0.41715
s_3	2.33126	-0.18070	2.86823	-0.18981	3.45426	-0.19587	4.08599	-0.20000
	0.29438	0.69233	0.37667	0.69535	0.46405	0.70063	0.55855	0.70391
	0.10701	0.41641	0.13662	0.41836	0.16789	0.41638	0.20181	0.41549
p_1	46.08301	0.10523	53.82375	0.10537	63.56607	0.10256	73.97547	0.10038
	10.17027	0.45932	12.00132	0.45997	14.22227	0.45658	16.60756	0.45381
	2.64594	0.61415	3.18754	0.61007	3.81975	0.61299	4.50454	0.61517
p_2	6.33123	-0.01765	8.24064	-0.01977	10.07949	-0.02174	11.99359	-0.02324
	0.45039	0.46854	0.58347	0.48043	0.73445	0.48665	0.90133	0.49092
	0.13218	0.63428	0.16444	0.62904	0.20415	0.62544	0.24967	0.62216

	K Expn.	K Coef.	Ca Expn.	Ca Coef.		K Expn.	K Coef.	Ca Expn.	Ca Coef.
s_1	1719.59267	0.06494	1913.72759	0.06469	s_4	0.24456	-0.15198	0.43143	-0.18129
	259.84607	0.38101	289.30205	0.38005		0.03646	0.69152	0.06191	0.65521
	56.61061	0.67715	63.08371	0.67806		0.01575	0.40415	0.02515	0.45250
s_2	74.93479	-0.09800	83.57226	-0.09897	p_1	85.80214	0.09763	97.81065	0.09611
	6.71595	0.65633	7.52856	0.66441		19.30666	0.44975	22.09133	0.44736
	2.68062	0.40988	3.02334	0.40161		5.28001	0.61915	6.09733	0.62073
s_3	4.63287	0.21433	5.33894	-0.22469	p_2	13.46751	-0.02403	15.20851	-0.02480
	0.71754	-0.66019	0.85441	0.67840		1.15059	0.48477	1.41369	0.48511
	0.28530	-0.46430	0.35650	0.44908		0.34456	0.61746	0.44538	0.61054

Table III. Exponents and expansion coefficients for MINI-3.

	Na		Mg		Al		Si	
	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.
s_1	1579.33764	0.01901	1881.67314	0.01902	2218.85864	0.01896	2570.07839	0.01903
	237.83356	0.13204	284.41190	0.13149	335.40180	0.13107	389.07064	0.13119
	53.48980	0.45907	64.19875	0.45755	75.88327	0.45634	88.29772	0.45580
	14.22567	0.52894	17.12278	0.53044	20.29496	0.53163	23.69936	0.53159
s_2	21.45916	-0.08571	25.87308	-0.08857	30.64061	-0.09127	35.84419	-0.09341
	1.94861	0.56946	2.41224	0.57731	2.94533	0.57980	3.51223	0.58829
	0.64045	0.50984	0.83389	0.49903	1.06071	0.49458	1.30118	0.48488
s_3	0.49202	-0.11559	0.87509	-0.12576	1.29276	-0.14674	1.74744	-0.16209
	0.05415	0.68349	0.10144	0.63565	0.16221	0.65648	0.22736	0.67309
	0.02135	0.39392	0.03716	0.45260	0.05945	0.44115	0.08315	0.43111
p_1	17.94519	0.12489	23.28368	0.12108	30.08925	0.11447	37.55529	0.10981
	3.81486	0.47971	5.01503	0.47895	6.56668	0.46982	8.25210	0.46489
	0.88032	0.60376	1.20650	0.59964	1.64223	0.60564	2.11193	0.60908
p_2					2.95562	-0.00983	4.62193	-0.01458
					0.24068	0.38471	0.33389	0.44632
					0.06912	0.71230	0.09687	0.65616

	P		S		Cl		Ar	
	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.
s_1	2948.54973	0.01908	3404.96838	0.01877	3848.12178	0.01877	4314.36298	0.01879
	446.45051	0.13144	515.52133	0.12963	583.13176	0.12947	654.57765	0.12937
	101.56620	0.45557	117.15110	0.45311	132.74171	0.45247	149.28981	0.45184
	27.35402	0.53121	31.50415	0.53526	35.76842	0.53576	40.30755	0.53618
s_2	41.49165	-0.09532	47.62582	-0.09691	54.16815	-0.09842	61.18994	-0.09950
	4.13819	0.59398	4.79975	0.60347	5.53537	0.60664	6.26800	0.62033
	1.56799	0.47840	1.84723	0.46843	2.16315	0.46488	2.46541	0.45105
s_3	2.25085	-0.17376	2.75897	-0.18327	3.35656	-0.19033	3.95559	-0.19531
	0.29792	0.68527	0.38496	0.67978	0.46909	0.69440	0.56857	0.69193
	0.10889	0.42344	0.14071	0.43472	0.17073	0.42279	0.20697	0.42848
p_1	46.08301	0.10527	53.98472	0.10501	63.79540	0.10213	74.07406	0.10024
	10.17027	0.45952	12.02830	0.45966	14.25929	0.45619	16.62276	0.45379
	2.64594	0.61394	3.19190	0.61070	3.82583	0.61375	4.50681	0.61534
p_2	6.33123	-0.01763	8.23121	-0.01984	10.10537	-0.02180	11.98143	-0.02324
	0.45039	0.46840	0.58376	0.47990	0.73448	0.48637	0.90145	0.49079
	0.13218	0.63442	0.16451	0.62956	0.20416	0.62570	0.24966	0.62232

	K		Ca			K		Ca	
	Expn.	Coef.	Expn.	Coef.		Expn.	Coef.	Expn.	Coef.
s_1	5012.79012	0.01792	5624.94666	0.01767	s_4	0.23945	0.14915	0.41390	-0.16967
	755.56898	0.12519	847.41005	0.12375		0.03640	-0.69701	0.06168	0.66700
	170.83815	0.44734	191.40949	0.44514		0.01575	-0.39841	0.02488	0.43944
	45.75608	0.54501	51.20373	0.54845					
					p_1	85.84990	0.09756	97.88503	0.09601
s_2	68.48170	-0.10110	76.78293	-0.10185		19.31809	0.44968	22.11151	0.44717
	7.18935	0.60909	7.99851	0.62429		5.28280	0.61925	6.10197	0.62097
	2.87950	0.46209	3.22022	0.44651					
					p_2	13.53275	-0.02409	15.27359	-0.02488
s_3	4.55644	-0.20885	5.25199	-0.21963		1.14840	0.48570	1.41123	0.48598
	0.71053	0.67474	0.84669	0.69358		0.34398	0.61653	0.44474	0.60965
	0.28242	0.44878	0.35313	0.43309					

Table IV. Exponents and expansion coefficients for MINI-4.

	Na Expn.	Na Coef.	Mg Expn.	Mg Coef.	Al Expn.	Al Coef.	Si Expn.	Si Coef.
s_1	1584.62613	0.01896	1878.63824	0.01905	2220.96184	0.01894	2581.38826	0.01893
	237.93226	0.13204	284.11346	0.13153	335.40618	0.13107	390.50243	0.13071
	53.48784	0.45899	64.18707	0.45735	75.86390	0.45638	88.51192	0.45541
	14.22088	0.52910	17.11882	0.53059	20.28413	0.53163	23.72339	0.53255
s_2	21.42052	−0.08586	25.86957	−0.08867	30.64994	−0.09129	35.78064	−0.09358
	1.94477	0.57234	2.40558	0.58078	2.93625	0.58299	3.51980	0.58666
	0.63758	0.50724	0.82946	0.49576	1.05426	0.49157	1.30161	0.48679
s_3	0.52440	−0.11339	0.90918	−0.12634	1.31578	−0.14841	1.75621	−0.16340
	0.05407	0.70084	0.10146	0.64488	0.16269	0.65887	0.22983	0.66613
	0.02106	0.37434	0.03698	0.44259	0.05946	0.43887	0.08409	0.43872
p_1	38.22544	0.04370	49.11481	0.04215	67.36412	0.03572	82.63764	0.03467
	8.52713	0.23443	11.09001	0.22979	15.29472	0.20630	18.80634	0.20378
	2.36602	0.51289	3.13902	0.51616	4.38339	0.50534	5.45008	0.50592
	0.64731	0.44280	0.89691	0.43473	1.28709	0.46254	1.64722	0.45887
p_2					4.27052	−0.00855	5.64039	−0.01147
					0.22965	0.42253	0.33106	0.46349
					0.06459	0.68105	0.09475	0.64160

	P Expn.	P Coef.	S Expn.	S Coef.	Cl Expn.	Cl Coef.	Ar Expn.	Ar Coef.
s_1	2952.46717	0.01905	3423.41131	0.01867	3855.56170	0.01873	4379.83516	0.01846
	447.22377	0.13114	516.87666	0.12937	584.23357	0.12920	663.38769	0.12767
	101.74040	0.45512	117.31748	0.45280	132.93186	0.45217	150.74592	0.45013
	27.37811	0.53198	31.52309	0.53591	35.79090	0.53636	40.52929	0.53976
s_2	41.44401	−0.09549	47.63257	−0.09656	54.15434	−0.09844	61.25439	−0.09961
	4.14795	0.59214	4.79276	0.59627	5.52527	0.60937	6.28070	0.61793
	1.56898	0.48049	1.83831	0.47574	2.15040	0.46242	2.46782	0.45359
s_3	2.26237	−0.17484	2.77567	−0.18823	3.34449	−0.19079	3.95647	−0.19594
	0.29976	0.68195	0.38467	0.67301	0.47494	0.68441	0.57301	0.68535
	0.10950	0.42719	0.14030	0.44277	0.17308	0.43372	0.20874	0.43561
p_1	97.51908	0.03471	115.12771	0.03410	131.59905	0.03449	152.61138	0.03368
	22.35582	0.20420	26.46023	0.20292	30.40899	0.20499	35.31198	0.20282
	6.56167	0.50704	7.81884	0.50851	9.05879	0.51141	10.55209	0.51225
	2.03529	0.45230	2.46658	0.44875	2.90681	0.44052	3.41986	0.43980
p_2	7.37347	−0.01337	9.30690	−0.01522	11.28714	−0.01652	13.40059	−0.01774
	0.45273	0.47940	0.59482	0.48462	0.75025	0.48988	0.91883	0.49558
	0.13089	0.62553	0.16512	0.62662	0.20510	0.62406	0.25042	0.61931

	K Expn.	K Coef.	Ca Expn.	Ca Coef.		K Expn.	K Coef.	Ca Expn.	Ca Coef.
s_1	5012.49720	0.01792	5622.34128	0.01768	s_4	0.23828	0.14941	0.41520	−0.17025
	755.53034	0.12517	846.96003	0.12380		0.03646	−0.69630	0.06157	0.66893
	170.85707	0.44723	191.31099	0.44524		0.01576	−0.39957	0.02483	0.43748
	45.75320	0.54515	51.17270	0.54832					
					p_1	176.05906	0.03275	202.98255	0.03153
s_2	68.48405	−0.10116	76.52458	−0.10206		40.87042	0.19887	47.10648	0.19460
	7.19166	0.60909	8.04094	0.61867		12.28523	0.51003	14.18286	0.50873
	2.87354	0.46229	3.23797	0.45242		4.01859	0.44382	4.66623	0.44796
s_3	4.56739	−0.20912	5.26751	−0.21989	p_2	15.14810	−0.01784	17.08207	−0.01837
	0.71123	0.67448	0.84626	0.69444		1.16433	0.49478	1.42216	0.49898
	0.28239	0.44910	0.35254	0.43216		0.34300	0.60921	0.44121	0.59816

Table V. Total energies (in a.u.).

Atom	STO–3G	MINI–1	MINI–3	MINI–4	44–31G[a]	SZ	DZ
Na(^{2}S)	−159.80299	−160.87646	−161.42257	−161.62333	---	−161.12392	−161.84999
Mg(^{1}S)	−197.18614	−198.45850	−199.10583	−199.33897	---	−198.85779	−199.60701
Al(^{2}P)	−239.02832	−240.55371	−241.31005	−241.56288	---	−241.15376	−241.87307
Si(^{3}P)	−285.56396	−287.33479	−288.20849	−288.49392	---	−288.08996	−288.85116
P(^{4}S)	−336.94520	−338.98472	−339.98396	−340.30633	−340.32016	−339.90988	−340.71595
S(^{3}P)	−393.17895	−395.53461	−396.66820	−397.03254	−397.05120	−396.62762	−397.50229
Cl(^{2}P)	−454.54620	−457.25788	−458.53384	−458.94610	−458.97140	−458.52369	−459.47960
Ar(^{1}S)	−521.22353	−524.32079	−525.74742	−526.21217	---	−525.76525	−526.81511
K(^{2}S)	---	−596.40362	−597.98890	−598.50067	---	−598.08987	−599.16241
Ca(^{1}S)	---	−673.71597	−675.46760	−676.02963	---	−675.63390	−676.75594

[a] Total energies given in this table, which were recalculated by restricted Hartree–Fock (HF) method, are slightly different from those given in ref. 4, because the values given by Pople's group were obtained with unrestricted HF method that does not give the energy of a pure state.

III. RESULTS AND DISCUSSION

The total energies of the MINI-i sets are given in Table V, together with those of STO-3G,[3] SZ,[5] DZ,[5] and 44-31G.[4] It is to be noted in Table V that the MINI-1 sets give much better total energies than the STO-3G sets, although the number of the primitive GTOs used in MINI-1 is the same as used in STO-3G. It is also seen that the total energy is greatly improved in going from MINI-1 to MINI-3, and the energies given by MINI-3 are lower than those of SZ for the atoms from Na through Cl. The MINI-4 sets give values fairly close to those given by DZ. The amount of decrease of the total energies in going from MINI-1 to MINI-3 is about three times as much as that in going from MINI-3 to MINI-4. It means that the addition of one primitive GTO to s_1 works more effectively in decreasing total energy in comparison with the addition to p_1.

The 44-31G sets have been published only for P, S, and Cl. These basis sets are to be compared with our MIDI-i sets. The total energies given by MIDI-4 are −340.31681, −397.04444, and −458.95843 a.u. for S, P, and Cl, respectively. They are very close to those given by 44-31G, although the size of MIDI-4 (4321/421) is much smaller than 44-31G (4431/431). The 44-31G sets have been

obtained by direct atomic energy optimization without going through STO functions. However, the 44-31G basis functions are constrained to use the same exponent for s- and p-type functions as it is for the STO-kG basis sets.

Now we turn to the discussion of atomic orbital energies. As mentioned in the Introduction, the MINI-i basis sets have been derived so as to represent the valence region of atoms more adequately by avoiding an "overspending" of the primitive GTOs in the inner-core region of atoms. Nevertheless, only the $1s$ orbital energies given by MINI-1 are slightly poorer than those of SZ, and MINI-3 and MINI-4 give comparable $1s$ orbital energy with SZ. Other orbital energies given by our basis sets are always far superior to those of SZ and close to the HF values.

In Figures 1 and 2, the error defined by the following equation is plotted against the atomic number Z, for the valence orbitals of the atoms Na through Ar.

$$\text{Error} = (|\epsilon_{\text{HF}} - \epsilon_i|/|\epsilon_{\text{HF}}|) \times 100\% \qquad (6)$$

where i = MINI-1, MINI-3, MINI-4, SZ, and 44-31G, and ϵ indicates an orbital energy. It is found that the errors for SZ are very large both for the $3s$ and the $3p$ orbitals. The errors for STO-3G are not shown in Figures 1 and 2. However, one would

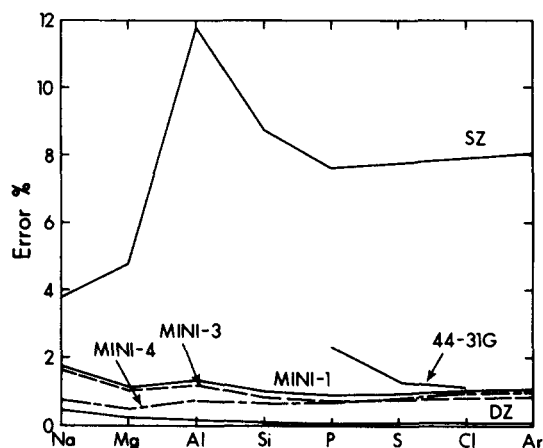Figure 1.   Error of the orbital energy for $3s$.

Figure 2.   Error of the orbital energy for $3p$.

naturally expect that the errors for STO-3G are larger than those for SZ because the STO-3G sets have been determined to simulate the SZ functions. All of MINI-i sets give excellent $3s$ orbital energies and the errors are around 1%. They are about one-half of the errors for the $2s$ orbital energies for the second-row atoms (Li–Ne). As for the $3p$ orbital, the error increases up from 1% (Al) to 3% (Ar) for MINI-1 and MINI-3, and the errors for MINI-4 are slightly less than those. For the second-row atoms, it has been found that the MINI-2 and the MINI-4 basis sets give much better $2p$ orbital energies than the MINI-1 and the MINI-3 basis sets, because one extra p GTO is used for p_1 in MINI-2 and MINI-4 compared with MINI-1 and MINI-3.[1] It is to be noted that MINI-1 and MINI-3 for the third-row atoms give nearly the same quality of the valence p orbital energies as MINI-2 and MINI-4 for the second-row atoms, although no extra p GTO is used for p_1 in MINI-1 and MINI-3. This is part of the reason for the omission of MINI-2 and MIDI-2 in the present work. It may be because the atoms treated here have two p-type atomic orbitals (i.e., $2p$ and $3p$) and each of them is represented by a linear combination of p_1 and p_2 through eq. (2), three primitive GTOs being used for each p_1 and p_2 in MINI-1 and MINI-3; therefore, six primitive GTOs are used in total for the $2p$ and the $3p$ orbitals. On the other
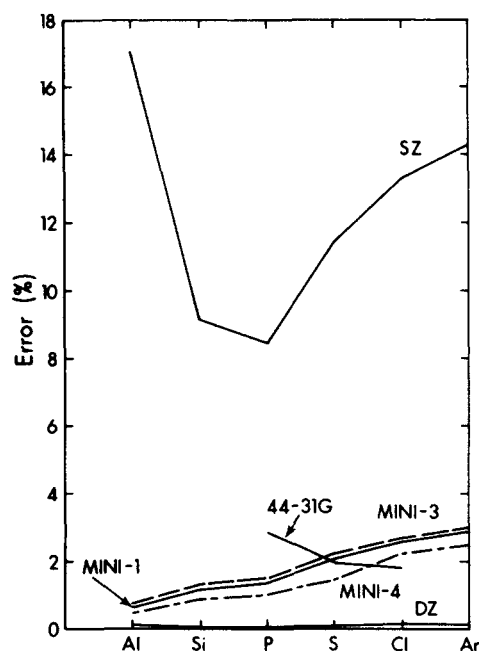
hand, the atoms of the second row have only one p-type atomic orbital, so that the $2p$ orbital in MINI-1 and MINI-3, being represented by three primitive GTOs, may not be enough to give the $2p$ orbital energy satisfactorily. An addition of one extra p GTO works efficiently to improve the $2p$ orbital energy for those atoms. The SMIDI-i and the MIDI-i sets give slightly better orbital energies than the MINI-i sets, while the data are not shown in Figures 1 and 2 to avoid complexity.

Finally, a few words about the 44-31G basis set. It is seen in Figures 1 and 2 that the orbital energies for S and Cl given by 44-31G are roughly the same as those given by our basis sets. However, the values of P show rather curious trends. It was noticed in the article by Hehre and Lathan[4] that the orbital exponents of valence shell orbital for P are out of line with that found in S and Cl. The exponents in our basis sets, given in Tables II–IV, lie on a smooth curve with respect to the atomic number Z.

The numerical data of the total energies for SMIDI-i and MIDI-i are not tabulated in this ar-

ticle. It has been found that the splitting of valence orbitals results in a rather minor improvement on the atomic total energy. It is to be noted, however, that our main purpose of constructing the SMIDI-i and the MIDI-i basis sets is to enhance flexibility of the basis sets for molecular calculations rather than to lower atomic total energies. In the following article, the validity of the basis sets obtained in the present article will be tested for the diatomic and the polyatomic molecules.

References

1. H. Tatewaki and S. Huzinaga, *J. Comput. Chem.*, **1**, 205 (1980).
2. H. Tatewaki and S. Huzinaga, *J. Chem. Phys.*, **71**, 4339 (1979).
3. W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **52**, 2769 (1970).
4. W. J. Hehre and W. A. Lathan, *J. Chem. Phys.*, **56**, 5255 (1972).
5. E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).