

# A Systematic Preparation of New Contracted Gaussian-Type Orbital Sets. VIII.

## MINI-1 and MIDI-1 Sets for Ga through Cd

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Minimal contracted Gaussian basis sets are presented for Ga through Cd. Characteristically these Gaussian-based minimal sets give far better *d* orbital energies than those by minimal STO basis sets. These new basis sets were tested on Br<sub>2</sub> for which a new benchmark calculation was also performed. The test result is satisfactory in that these basis sets produce good general agreement with the near Hartree-Fock calculation with respect to the molecular spectroscopic constants.

### I. INTRODUCTION

A variety of compact contracted Gaussian-type (CGTO) basis sets have been prepared for Li through Zn.<sup>1-3</sup> This article is a continuation of that work. Minimal-type basis sets are presented for Ga through Cd. They are termed MINI-1 in accordance with our previously adopted nomenclature.<sup>1</sup> Three primitive GTOs are used for each of the CGTOs in MINI-1. Orbital exponents and contraction coefficients were determined by optimizing total energies as was explained in detail in a previous article.<sup>3</sup>

For the first-row transition metal atoms, the MINI-1 basis sets were shown to give far better 3*d* orbital energies than those by the STO SZ basis sets,<sup>3,4</sup> but the magnitude of errors for 3*d* still remained large in comparison with those for *p* and *s* orbital energies. For the second-row transition metal atoms, however, the MINI-1 basis sets turn out to be capable of producing *d* orbital energies in equally good accuracy as *p* and *s* orbital energies, while performance of STO SZ sets still remains rather poor.

The split-type basis sets, MIDI-1, are derived

from MINI-1 in much the same way as done in the previous article.<sup>1,2</sup> MINI-1, MIDI-1, and some other related basis sets were tested in a series of *ab initio* molecular orbital calculations on the Br<sub>2</sub> molecule. For testing purposes we have carried out a new benchmark calculation on Br<sub>2</sub> using a large GTO basis set. The test result seems quite satisfactory and encourages the use of MINI-1 and MIDI-1 basis sets for molecular calculations.

### II. ATOMIC WAVEFUNCTIONS

#### A. MINI-1

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

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

$$N = 4 \text{ for Ga to Kr and } N = 5 \text{ for Rb to Cd} \quad (1)$$

$$R_{np}(r) = \sum_{i=1}^N C_{np,i} p_i(r), \quad N = 3 \quad (2)$$

$$R_{nd}(r) = \sum_{i=1}^N C_{nd,i} d_i(r),$$

$$N = 1 \text{ for Ga to Sr and } N = 2 \text{ for Y to Cd} \quad (3)$$

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where  $n$  is the principal quantum number. In the MINI-1 sets, three primitive Gaussian-type functions (GTOs) are used to construct each  $s_i(r)$ ,  $p_i(r)$ , or  $d_i(r)$ , which can be written as

$$s_i(r) = \sum_{k=1}^3 d_{s_i,k} g_{s_i}(\alpha_{s_i,k}, r) \quad (4)$$

$$p_i(r) = \sum_{k=1}^3 d_{p_i,k} g_{p_i}(\alpha_{p_i,k}, r) \quad (5)$$

$$d_i(r) = \sum_{k=1}^3 d_{d_i,k} g_{d_i}(\alpha_{d_i,k}, r) \quad (6)$$

where  $g_{s_i}$ ,  $g_{p_i}$ , and  $g_{d_i}$  are normalized  $1s$ -type,  $2p$ -type, and  $3d$ -type Gaussian functions, respectively. The convenient shorthand notations are (3333/333/3) for Ga to Kr, as (33333/333/3) for Rb and Sr, and (33333/333/33) for Y to Cd. The orbital exponents and the contraction coefficients have been determined in the same method reported elsewhere,<sup>3</sup> and the values are shown in Table I.

## B. MIDI-1

The MIDI-1 basis set can be described as (33321/33321/3) for Ga through Kr, as (333321/333/3) for Rb and Sr, and (333321/333/321) for Y through Cd. These basis sets were obtained merely by splitting the valence shell orbitals of parent MINI-1 sets into two parts without changing any exponents and contraction coefficients given in Table I. If more flexibility is required for molecular calculations we may split all the outermost orbitals of  $s$ ,  $p$ , and  $d$  types. Renormalization is, of course, necessary for each orbital.

## C. Total and Orbital Energies

Total energies given by MINI-1 are given in Table II together with those given by STO SZ and DZ.<sup>5</sup>

MINI-1 give shallower total energies than STO SZ. If we are interested in getting total energies

**Table I.** Exponents and expansion coefficients for MINI-1.

	Ga ( <sup>2</sup> P)		Ge ( <sup>3</sup> P)		As ( <sup>4</sup> S)		Se ( <sup>3</sup> P)	
	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.
$s_1$	4734.41355	0.06309	5051.83305	0.06300	5373.14930	0.06302	5715.38313	0.06291
	717.03507	0.37424	765.60521	0.37380	814.78055	0.37369	866.51303	0.37333
	157.21175	0.68356	167.92334	0.68395	178.87522	0.68395	190.30059	0.68429
$s_2$	210.73599	-0.10547	224.89110	-0.10575	239.79458	-0.10606	255.23194	-0.10632
	19.80157	0.70740	21.17763	0.71096	22.62844	0.71297	24.11743	0.71498
	8.05193	0.35963	8.60725	0.35613	9.19347	0.35423	9.81016	0.35219
$s_3$	16.35935	-0.22833	17.80747	-0.22737	19.15505	-0.22929	20.57072	-0.23096
	2.65530	0.71475	2.83908	0.73090	3.04553	0.74777	3.26003	0.76658
	1.06085	0.41843	1.15055	0.39992	1.24742	0.38296	1.34144	0.36426
$s_4$	1.36765	-0.15175	1.56709	-0.17525	1.80148	-0.19726	1.99401	-0.21281
	0.17557	0.63645	0.22753	0.65370	0.28185	0.66024	0.34561	0.65746
	0.06392	0.46415	0.08390	0.45949	0.10550	0.46353	0.13017	0.47783
$p_1$	274.38968	0.09025	293.42083	0.09040	314.18656	0.09024	334.71076	0.09028
	62.99802	0.44471	67.61106	0.44478	72.50029	0.44456	77.57597	0.44372
	18.18102	0.61916	19.57164	0.61848	21.05251	0.61828	22.61235	0.61840
$p_2$	49.28530	-0.02996	51.45157	-0.02837	54.49322	-0.02795	58.64604	-0.02808
	4.87363	0.49982	5.48857	0.48023	6.05515	0.47159	6.58902	0.46930
	1.54803	0.59638	1.76997	0.61319	1.98879	0.61908	2.20366	0.61892
$p_3$	3.50273	-0.01665	3.74397	-0.02791	4.03778	-0.03641	4.50393	-0.04306
	0.22420	0.40308	0.27991	0.47089	0.34465	0.50577	0.41935	0.51696
	0.06333	0.69855	0.08399	0.63015	0.10735	0.59335	0.12751	0.58734
$d_1$	21.01067	0.16409	24.19805	0.15871	27.29366	0.15545	30.33647	0.15381
	5.35109	0.51096	6.19837	0.51173	7.05451	0.51179	7.90696	0.51289
	1.32896	0.58838	1.58341	0.58485	1.84965	0.58110	2.12105	0.57605

Table I (continued)

	Br ( $^2P$ )		Kr ( $^1S$ )		Rb ( $^2S$ )		Sr ( $^1S$ )	
	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.
$s_1$	6056.16497	0.06292	6403.47848	0.06300	6798.68464	0.06267	7168.17620	0.06272
	918.96445	0.37320	972.11100	0.37324	1031.18763	0.37233	1087.95601	0.37229
	201.95153	0.68434	213.90882	0.68414	226.72378	0.68521	239.43879	0.68512
$s_2$	271.08548	-0.10659	286.63799	-0.10690	303.82934	-0.10710	321.01596	-0.10735
	25.64521	0.71758	27.30120	0.71661	28.91348	0.71895	30.61798	0.71972
	10.42605	0.34967	11.12031	0.35081	11.79429	0.34833	12.51542	0.34754
$s_3$	22.00266	-0.23334	23.35643	-0.23725	24.98156	-0.23841	26.49582	-0.24161
	3.51591	0.77093	3.78626	0.77893	4.03664	0.79345	4.33825	0.79640
	1.47196	0.36035	1.59752	0.35441	1.71074	0.33979	1.85991	0.33841
$s_4$	2.29982	-0.23248	2.54821	-0.24458	2.87318	0.26899	3.19349	0.28985
	0.39404	0.69098	0.45455	0.70001	0.51589	-0.74611	0.58231	-0.79667
	0.14891	0.45098	0.17236	0.44933	0.21026	-0.40879	0.24611	-0.36593
$s_5$					0.18298	0.16877	0.34953	0.21208
					0.03788	-0.53007	0.05049	-0.71101
					0.01682	-0.58362	0.02089	-0.40637
$p_1$	357.75879	0.08978	380.87992	0.08957	403.69176	0.08965	428.64434	0.08930
	82.99850	0.44305	88.48672	0.44246	94.00665	0.44229	99.98830	0.44129
	24.22208	0.61909	25.90023	0.61930	27.61504	0.61885	29.44175	0.61960
$p_2$	58.80826	-0.02696	63.25696	-0.02702	66.84737	-0.02732	70.21220	-0.02748
	7.38264	0.45008	7.95380	0.45070	8.61285	0.44641	9.30971	0.44225
	2.48846	0.63644	2.72394	0.63383	2.99560	0.63608	3.28131	0.63852
$p_3$	4.91469	-0.05456	5.39516	-0.06079	5.88651	-0.06536	6.37433	-0.06882
	0.49001	0.53523	0.56568	0.54950	0.66752	0.56989	0.77594	0.58753
	0.14913	0.57153	0.17336	0.55797	0.22333	0.52709	0.27408	0.50368
$d_1$	33.65964	0.15137	37.11330	0.14929	40.74243	0.14722	44.44350	0.14569
	8.83353	0.51292	9.79757	0.51317	10.81593	0.51299	11.85644	0.51331
	2.41386	0.57342	2.72046	0.57091	3.04633	0.56918	3.38306	0.56693

	Y ( $^2D$ )		Zr ( $^3F$ )		Nb ( $^6D$ )		Mo ( $^7S$ )	
	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.
$s_1$	7646.54686	0.06190	8091.57553	0.06152	8462.16233	0.06184	8893.77639	0.06175
	1156.48810	0.37034	1222.35237	0.36930	1280.70714	0.36992	1346.18544	0.36953
	253.66802	0.68762	267.78250	0.68887	281.17818	0.68793	295.58720	0.68832
$s_2$	339.25556	-0.10752	358.28747	0.10760	375.98738	0.10800	395.55716	0.10808
	32.33314	0.72171	33.99419	-0.72755	36.02687	-0.72163	37.85443	-0.72372
	13.19845	0.34561	13.82193	-0.33973	14.76801	-0.34570	15.48815	-0.34366
$s_3$	28.14338	-0.24383	29.92585	-0.24448	31.45914	-0.24901	33.28502	-0.24963
	4.61767	0.80904	4.86079	0.83513	5.23758	0.82425	5.53855	0.83462
	1.98973	0.32644	2.06110	0.30042	2.28040	0.31375	2.39993	0.30375
$s_4$	3.52328	0.30368	3.85239	-0.31103	4.16157	0.31516	4.50176	-0.32135
	0.66088	-0.80432	0.73421	0.82268	0.82176	-0.80469	0.90160	0.81151
	0.28219	-0.36575	0.31201	0.35238	0.34317	-0.37647	0.37414	0.37407
$s_5$	0.43043	0.21985	0.49679	-0.21791	0.57325	0.21915	0.65463	-0.21703
	0.05676	-0.71871	0.06432	0.70789	0.06685	-0.68648	0.07346	0.65798
	0.02283	-0.39672	0.02540	0.40696	0.02620	-0.42232	0.02841	0.44857
$p_1$	463.18703	0.08668	490.62393	0.08625	517.92436	0.08616	545.81023	0.08602
	107.71430	0.43653	114.26076	0.43534	120.61760	0.43541	127.31995	0.43485
	31.60437	0.62600	33.58589	0.62705	35.54645	0.62666	37.59737	0.62694
$p_2$	72.11967	-0.02784	76.32777	-0.02817	82.65639	-0.02869	86.07180	-0.02824
	10.21290	0.42750	10.94733	0.42509	11.50209	0.43360	12.36927	0.42694
	3.62596	0.65186	3.92986	0.65291	4.18622	0.64320	4.52531	0.64891
$p_3$	6.87643	-0.07092	7.41492	-0.07757	7.96180	-0.07312	8.72443	-0.07894
	0.89761	0.58442	0.99682	0.60120	1.12239	0.59302	1.22256	0.60529
	0.32154	0.50658	0.35952	0.49061	0.39650	0.50174	0.43315	0.49003
$d_1$	50.20651	0.13739	54.74788	0.13473	58.90744	0.13397	63.62405	0.13217
	13.48765	0.50268	14.78336	0.50035	15.97346	0.50076	17.32439	0.49940
	3.93233	0.57778	4.35912	0.57914	4.75368	0.57716	5.20606	0.57745
$d_2$	1.46306	0.17864	1.82597	0.17916	2.12022	-0.18097	2.37857	-0.19386
	0.58114	0.37061	0.62995	0.49025	0.67706	-0.51490	0.76519	-0.53015
	0.20319	0.62799	0.19594	0.53704	0.18964	-0.53530	0.21933	-0.50456

Table I (continued)

	Tc ( $^6S$ )		Ru ( $^5D$ )		Rh ( $^4F$ )		Pd ( $^3F$ )	
	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.	Expn.	Coef.
$s_1$	9308.51311	0.06186	9762.42755	0.06176	10168.67800	0.06204	10617.05300	0.06211
	1410.27943	0.36968	1478.94003	0.36936	1543.46969	0.36984	1612.55164	0.36989
	310.00996	0.68802	325.11374	0.68835	339.93137	0.68759	355.42988	0.68743
$s_2$	414.51989	0.10837	435.79809	0.10847	455.18478	0.10873	475.82299	0.10890
	39.84895	-0.72405	41.73579	-0.72779	43.87346	-0.72620	45.95156	-0.72719
	16.36004	-0.34331	17.11364	-0.33945	18.02635	-0.34122	18.92352	-0.34016
$s_3$	35.18833	-0.25104	36.98192	-0.25388	38.91606	-0.25534	40.88737	-0.25686
	5.80761	0.86326	6.18247	0.86223	6.50293	0.87730	6.84073	0.88892
	2.45072	0.27594	2.64082	0.27857	2.73084	0.26461	2.84227	0.25396
$s_4$	4.88475	-0.32361	5.24896	-0.32655	5.61933	-0.32787	6.01395	-0.32853
	0.98099	0.83276	1.06822	0.83630	1.15960	0.83561	1.25526	0.83129
	0.41423	0.35356	0.44949	0.35297	0.48773	0.35588	0.52935	0.36161
$s_5$	0.66696	-0.19285	0.72301	-0.18442	0.76938	-0.17330	0.84107	-0.17355
	0.08235	0.66652	0.08878	0.65667	0.09520	0.64125	0.10050	0.63436
	0.03139	0.44085	0.03341	0.44896	0.03544	0.46233	0.03716	0.46803
$p_1$	575.73023	0.08561	609.37087	0.08473	639.89385	0.08458	670.01554	0.08469
	134.44586	0.43389	142.18142	0.43218	149.47131	0.43174	156.61377	0.43215
	39.74762	0.62785	42.05361	0.62986	44.28510	0.63008	46.49444	0.62934
$p_2$	88.80042	-0.02863	94.05284	-0.02914	100.06831	-0.02962	102.36581	-0.02932
	13.26387	0.42324	14.10237	0.42054	14.77666	0.42683	15.87528	0.41838
	4.88241	0.65198	5.23451	0.65364	5.54210	0.64653	5.95619	0.65468
$p_3$	9.24648	-0.08493	9.96347	-0.09127	10.60883	-0.08966	11.32390	-0.09817
	1.35111	0.61070	1.45824	0.62289	1.59637	0.62097	1.71267	0.62893
	0.49111	0.48342	0.53067	0.47227	0.58082	0.47466	0.62412	0.46836
$d_1$	68.39346	0.13074	73.77392	0.12830	78.88641	0.12701	83.87933	0.12643
	18.72078	0.49768	20.23333	0.49578	21.71417	0.49472	23.16072	0.49480
	5.68803	0.57761	6.18422	0.57958	6.68261	0.57985	7.17487	0.57869
$d_2$	2.55438	0.22506	2.82333	0.23423	3.12134	-0.24035	3.32885	-0.25612
	0.84792	0.55642	0.93494	0.55917	1.03115	-0.56233	1.09962	-0.56670
	0.26692	0.42967	0.29122	0.42118	0.31987	-0.41334	0.34122	-0.39447

	Ag ( $^2D$ )		Cd ( $^1S$ )	
	Expn.	Coef.	Expn.	Coef.
$s_1$	11132.04700	0.06183	11642.86600	0.06167
	1689.14072	0.36917	1765.63136	0.36871
	371.97182	0.68831	388.67995	0.68884
$s_2$	498.52302	0.10902	519.57443	0.10925
	48.02736	-0.72984	50.34785	-0.72686
	19.69818	-0.33765	20.74846	-0.34066
$s_3$	42.85646	-0.25899	44.72610	-0.26259
	7.22675	0.89260	7.70343	0.87938
	3.00079	0.25175	3.30829	0.26693
$s_4$	6.43796	-0.32866	6.80698	-0.33275
	1.34580	0.83322	1.46122	0.82012
	0.56674	0.36005	0.61611	0.37760
$s_5$	0.89644	-0.16527	0.90799	-0.14946
	0.10418	0.64081	0.11289	0.60191
	0.03800	0.45918	0.04094	0.49650
$p_1$	702.68354	0.08441	741.36190	0.08334
	164.46615	0.43135	173.37779	0.42944
	48.86936	0.63007	51.42797	0.63266
$p_2$	105.52626	-0.02959	103.19923	-0.02984
	16.87123	0.41462	18.45493	0.39529
	6.35646	0.65798	6.88682	0.67790
$p_3$	12.06102	-0.10190	12.71306	-0.11088
	1.84203	0.63204	1.99280	0.62401
	0.67149	0.46627	0.73043	0.47652
$d_1$	89.31070	0.12526	94.99985	0.12393
	24.73402	0.49381	26.38241	0.49253
	7.70690	0.57906	8.26172	0.57996
$d_2$	3.68020	-0.25628	4.01795	-0.25796
	1.21609	-0.56737	1.33278	-0.56716
	0.37661	-0.39381	0.41373	-0.39167

**Table II.** Total energies (in a.u.).

Atom	State	MINI-1	SZ <sup>a</sup>	DZ <sup>b</sup>
Ga	2p	-1914.9825	-1916.5167	-1923.1110
Ge	3p	-2066.6059	-2068.5139	-2075.2284
As	4s	-2224.9857	-2227.2649	-2234.1207
Se	3p	-2390.0932	-2392.7274	-2399.7563
Br	2p	-2562.1269	-2565.1131	-2572.3415
Kr	1s	-2741.1811	-2744.5197	-2751.9613
Rb	2s	-2926.9241	-2930.6931	-2938.2708
Sr	1s	-3119.5363	-3123.7176	-3131.4652
Y	2d	-3319.1984	-3324.7806	-3331.6538
Zr	3f	-3525.9125	-3531.3181	-3538.9632
Nb	6d	-3739.8616	----- <sup>c</sup>	-3753.5591
Mo	7s	-3961.1736	----- <sup>c</sup>	-3975.5121
Tc	6s	-4189.7958	-4196.0536	-4204.7590
Ru	5d	-4425.8149	-4432.3604	-4441.4569
Rh	4f	-4669.4301	-4676.2637	-4685.7699
Pd	3f	-4920.6953	-4927.8059	-4937.7504
Ag	2d	-5179.6989	-5187.0705	-5197.4836
Cd	1s	-5446.5644	-5454.1908	-5465.0971

<sup>a,b</sup> From single-zeta (SZ) calculation and double-zeta (DZ) calculations in ref. 5.

<sup>c</sup> No data are available in ref. 5.

better than those of STO SZ, all we have to do is add one more *s*-type primitive GTO to the innermost *s*-type CGTO. For example, the (4333/333/3) basis set, termed MINI-3 according to our convention,<sup>1</sup> for the Br atom gives the total energy of -2567.3767 a.u., which is a good deal lower than -2565.1131 a.u. given by the STO SZ set.

As for orbital energies, the values given by MINI-1 are much better than those given by STO SZ except for 1s orbitals. Percentage error defined by the following formula may be used as an indicator of the accuracy of calculated orbital energies  $\epsilon_i$  relative to the Hartree-Fock values  $\epsilon_{HF}$ ,

$$\text{Error} = [|\epsilon_{HF} - \epsilon_i|/|\epsilon_{HF}|] \times 100\% \quad (7)$$

where *i* may distinguish MINI-1, SZ, and DZ. The average values of percentage errors for the valence orbitals are summarized in Table III. The errors for the first transition metal atoms are also included in the table for easy comparison. Figure 1 is a graphic presentation of the percentage errors for *d*-type valence orbital energies. Anomalies at Nb and Mo are due primarily to the fact that we have chosen the electronic configuration 4d<sup>4</sup>5s instead of 4d<sup>3</sup>5s<sup>2</sup> for Nb and likewise 4d<sup>5</sup>5s instead of 4d<sup>4</sup>5s<sup>2</sup> for Mo. These open-5s configurations yield lower total energies than the closed-5s configurations.

Table III shows that STO SZ basis sets fail to give reasonable *d* valence orbital energies for all the

**Table III.** Average of the percentage errors for the valence orbital energies (in %).<sup>a</sup>

basis sets	Cr-Zn	Ga-Sr	Y-Cd <sup>b</sup>
<b>d orbital<sup>c</sup></b>			
SZ	75.2	36.9	97.3
MINI-1	16.2	7.0	2.4
MINI-2	4.8	----	----
DZ	4.4	1.5	1.2
<b>s orbital<sup>d</sup></b>			
SZ	15.8	14.6	23.2
MINI-1	4.8	2.2	1.9
MINI-2	2.6	----	----
DZ	2.5	0.9	1.5
<b>p orbital<sup>e</sup></b>			
SZ	9.9	15.7	11.9
MINI-1	2.7	2.4	1.0
MINI-2	1.7	----	----
DZ	0.9	1.0	0.4

<sup>a</sup> The values for SZ and DZ were calculated by using the data given in ref. 5. The data for Cr to Zn were taken from ref. 3, STD-SET(1) and DZC-SET(1) are renamed MINI-1 and MINI-2, respectively, in this article.

<sup>b</sup> The error of Nb (6d) and Mo (7s) are excluded for all of the basis sets, because no data are available for SZ calculation. See text for details.

<sup>c</sup> *d* is an abbreviation of 3d for Cr to Sr and 4d for Y to Cd.

<sup>d</sup> *s* is an abbreviation of 4s for Cr to Kr and 5s for Ru to Cd.

<sup>e</sup> *p* is an abbreviation of 4p for Cr to Cd.

atoms listed. Especially troublesome is yttrium for which the value given by SZ is +0.74275 a.u. while the Hartree-Fock value is -0.24987 a.u. The average percentage error (97.3%) reduces to 47.8% if yttrium is excluded. Compared to STO SZ, MINI-1 give far better values to all types of valence orbital energies. In fact, MINI-1 yield fairly close values to those given by STO DZ for the second-row transition metal atoms. This is in contrast to the fact that for the first-row transition metal atoms MINI-1 performance is not quite as good as that of DZ for the 3d orbital energies, although it is much better than that of SZ.

### III. MOLECULAR CALCULATIONS ON Br<sub>2</sub>

MINI-*i*, MIDI-*i*, and MIDI-*i*\* (*i* = 1 and 3) have been used for *ab initio* molecular calculations on

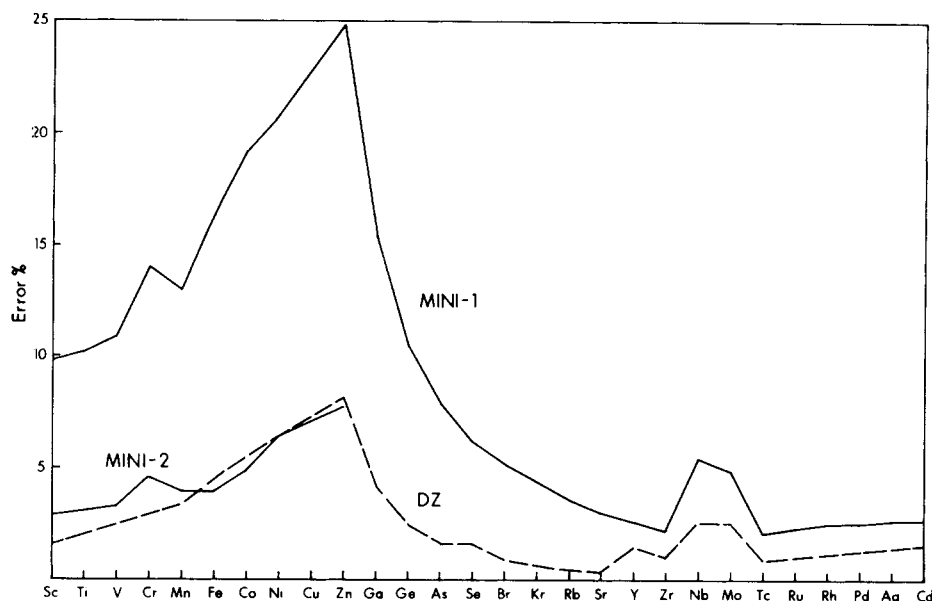


Figure 1. A graphic presentation of the percentage errors for  $d$ -type valence orbital energies.

$\text{Br}_2$  ( $^1\Sigma_g^+$ ) to test their effectiveness in molecular calculations. MINI-3 basis set parameters are given in Table IV. The asterisk indicates the addition of one  $d$ -type polarization function. All calculations are within the framework of the restricted Roothaan–Hartree–Fock self-consistent field (SCF) method and performed by a modified version<sup>6</sup> of the MOLECULE program originally developed by Almlöf.<sup>7</sup>

A large basis set with one  $d$ -type polarization function was also used to produce a reference calculation on  $\text{Br}_2$ . The basis set was derived from Huzinaga's (14s, 11p, 5d) primitive GTO basis set<sup>8</sup> and the contraction pattern is (5111111111/5111111/411). The total atomic energy given by this basis set is  $-2572.3810$  a.u., while STO DZ gives  $-2572.3415$  a.u. and the Hartree–Fock value is  $-2572.4408$  a.u. In the  $\text{Br}_2$  molecular calculation one  $d$ -type polarization function is added and the exponent was determined by maximizing the radial overlap integral between the polarization function and the valence orbitals,  $s_4$  and  $p_3$  of MINI-1 in Table I, and the value thus obtained, 0.43, was used for MIDI-1\*, MIDI-3\*, and the large basis set.

The total energy (t.e.), the atomization energy (a.e.), the bond length ( $r_e$ ), and other spectroscopic constants (the vibrational constant  $\omega_e$ , the rota-

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

$\text{Br } ({}^2\text{P})$		
	Expn.	Coef.
$s_1$	17548.57600	0.01744
	2662.93450	0.12092
	608.75893	0.43713
	164.73326	0.55694
$s_2$	249.60059	-0.10962
	27.27452	0.67179
	11.29386	0.40031
$s_3$	21.66133	-0.23543
	3.52265	0.77236
	1.48875	0.36049
$s_4$	2.29982	-0.22710
	0.39404	0.69205
	0.14891	0.44808
$p_1$	358.38429	0.08959
	83.09605	0.44281
	24.24066	0.61949
$p_2$	58.86345	-0.02710
	7.36869	0.45108
	2.48501	0.63544
$p_3$	4.91466	-0.05438
	0.48979	0.53536
	0.14902	0.57143
$d_1$	33.71618	0.15102
	8.84532	0.51264
	2.41595	0.57400

**Table V.** Total energy, atomization energy, geometry, and spectroscopic constants of  $\text{Br}_2$  ( $^1\Sigma_g^+$ ).<sup>a</sup>

Basis sets	t.e. (a.u.)	a.e. (a.u.) <sup>b</sup>	$r_e$ (Å)	$\omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$\kappa_e$ (dyn/cm)
MINI-1	-5124.2793	0.0023	2.448	353	0.0704	$2.93 \times 10^5$
MINI-3	-5134.7721	0.0001	2.479	330	0.0688	2.57
MIDI-1	-5124.4060	0.0014	2.458	305	0.0698	2.19
MIDI-3	-5134.9962	0.0018	2.458	308	0.0699	2.23
MIDI-1*	-5124.8886	0.0382	2.274	360	0.0816	3.04
MIDI-3*	-5135.3138	0.0342	2.281	355	0.0811	2.96
Extended <sup>c</sup>	-5144.7294	0.0298	2.287	352	0.0806	2.91
Extended <sup>d</sup>	-5144.7261	0.0925 <sup>f</sup>	2.29	358	---	3.02
Exptl. <sup>e</sup>		0.0732	2.284	323	0.0809	2.46

<sup>a</sup> 4s and 4p orbitals are split in MIDI-1, MIDI-1\*, MIDI-3\*, while in MIDI-3, all of 4s, 4p, and 3d orbitals are split.

<sup>b</sup> In order to calculate atomization energy, the atomic energy is corrected with additional 3s orbital<sup>1</sup> which inevitably appears in molecular calculations when six-membered  $d$  functions ( $x^2, y^2, z^2, xy, yz, zx$ )  $e^{-\gamma r^2}$  are employed. The atomic energies thus obtained are -2562.1385 (MINI-1), -2567.3860 (MINI-3), -2562.2023 (MIDI-1), -2567.4972 (MIDI-3), -2562.4252 (MIDI-1\*), -2567.6398 (MIDI-3\*), and -2572.3498 (extended basis) (in a.u.).

<sup>c</sup> This calculation has been done by the present authors. See text for details.

<sup>d</sup> See ref. 9.

<sup>e</sup> G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1950.

<sup>f</sup> A typographical error is suspect here. A near Hartree-Fock atomization energy is not expected to be larger than the experimental value.

tional constant  $B_e$ , and the force constant  $\kappa_e$ ) have been calculated. The calculational result is shown in Table V, where those of Straub and McLean<sup>9</sup> are also included. Their basis set consists of STO DZ plus two 4d- and two 4f-type polarization functions.

In the MINI-1 calculation scaling factors were used for  $d_1$ ,  $s_4$ , and  $p_3$  to optimize the molecular calculation, and their values were found to be 0.999, 1.003, and 1.015, respectively. The fact that they are all nearly equal to 1.0 suggests that scaling of orbital exponents would not be necessary for molecular calculations. It may be recalled that MINI- $i$  and MIDI- $i$  were shown to be capable of producing quite satisfactory results *without* using scale factors for a number of *ab initio* calculations on molecules containing various third-row atoms.<sup>10</sup> Accordingly, no scale factor is used for the basis sets listed in Table V except for MINI-1.

The  $s_4$  and the  $p_3$  of MINI- $i$  (before scaling) are

split to create MIDI-1, MIDI-1\*, and MIDI-3\*, while in MIDI-3 splitting is done also in  $d_1$  as well as  $s_4$  and  $p_3$ . From Table V we may conclude that the effect of splitting the 3d orbital is negligible. The only difference between the basis sets with  $i = 1$  and  $i = 3$  is that  $i = 1$  means there are three primitive GTCs in the innermost orbital  $s_1$  while  $i = 3$  means there are four primitive GTOs in  $s_1$ . The numerical results for  $r_e$ ,  $\omega_e$ ,  $B_e$ , and  $\kappa_e$  in Table V show a clear grouping tendency of MINI- $i$ , MIDI- $i$ , and MIDI- $i^*$  with  $i = 1$  and 3. We have already observed the same situation in our previous works.<sup>1,10</sup> It should also be noted that MIDI- $i^*$  give excellent agreement with the large basis set calculation in all aspects of molecular properties computed here.

A more convincing benchmark would be a metal diatomic like  $\text{Ag}_2$ , but the high computing cost has prevented us from carrying out such calculations.

#### IV. CONCLUDING REMARKS

Among many interesting observations that can be made in the present work the most gratifying observation would be that the MIDI-*i*\* basis sets produce numerical results consistently close to those by much more extended basis sets except for, of course, the total atomic and molecular energies. This finding is a repetition of our previous experiences in the present series of works. We feel confident that the MIDI-*i*\* could be recommended for a wide range of serious *ab initio* molecular calculations, although the testing could never be claimed to be complete. Another pleasant observation is the good performance of the minimal-type basis sets MINI-1. It should be regarded as somewhat fortuitous in the tradition of STO-3G but here again we stress the fact that our MINI-1 basis sets are far superior to STO SZ in representing

valence orbitals, especially *d*-type orbitals, properly.

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