A comparison of the geometrical sequence formula and the well-tempered formulas for generating GTO basis orbital exponents

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The geometrical sequence formula to generate orbital exponents of GTO basis sets is compared with other two generating formulas termed as well-tempered, for atoms from He to Cd.

Optimization of orbital exponents of Gaussian basis function sets becomes increasingly difficult and expensive for heavier atoms if we attempt to optimize a large number of exponents individually. Ruedenberg and coworkers [1] proposed the use of even-tempered basis sets, in which the values of orbital exponents $\{\zeta_{lk}\}$ are generated by a geometric sequence depending on two parameters, α_l and β_l for each angular symmetry l,

$$\zeta_{lk}=\alpha_l\beta_l^{k-1}\,,\quad \alpha_l,\beta_l>0\,,\quad \beta_l\neq 1\,,$$
$$k=1,2,...,n_l\,. \qquad (1)$$

Hence, the total number of variable parameters to be optimized is greatly reduced. For example, for any atoms with s, p, and d shells, there are only $2\times 3=6$ parameters to be optimized, regardless of the size of the basis set.

Bardo and Ruedenberg [2] and Clementi and Corongiu [3] used only two parameters α and β dropping their l dependency:

$$\zeta_k=\alpha\beta^{k-1}\,,\quad \alpha,\beta>0\,,\quad \beta>1\,,$$
$$k=1,2,...,n\,. \qquad (2)$$

In the present communication, this formula is called the geometrical formula.

An extension of formula (2) by adding two more parameters in the form

$$\zeta_k=\alpha\beta^{k-1}\left[1+\gamma\left(\frac{k-1}{n}\right)^{\delta}\right],\quad k=1,2,...,n\,, \qquad (3)$$

was used by Huzinaga, Klobukowski, and Tatwaki [4]. The GTO basis sets generated by using formula (3) are called well-tempered, emulating the even-tempered basis set by Ruedenberg. We shall call the above formula as the well-tempered formula 1, WT-F1. The formula has been used extensively to prepare large GTO basis sets [5].

Recently, we have been using another, similar generating formula,

$$\zeta_k=\zeta_{k-1}\beta\left[1+\gamma\left(\frac{k}{n}\right)^{\delta}\right],\quad k=2,...,n\,,$$
$$\zeta_0=\alpha\,,\quad \zeta_1=\alpha\beta\,. \qquad (4)$$

We call this system of recursive formulas as the well-tempered formula 2, WT-F2.

The purpose of the present note is to compare the effectiveness of the geometries sequence formula, WT-F1 and WT-F2 for atoms from He ($Z=2$) to Cd ($Z=48$).

A preliminary test was done with He. As a reference, van Duijneveldt's 7s, 8s, 9s and 10s expansions [6] were used, where the orbital exponents were individually optimized. Table 1 shows the total energies, and the optimized exponents are given in table 2. It is seen that WT-F2 works very well both in re-

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spect to the total energy and the orbital exponents.

Table 3 summarizes our effort so far to apply WT-F2 to atoms from He through Cd. We have been aiming at a level of accuracy comparable to that of Clementi in his recent compilation [7]. Reduction of the size of basis set achieved by the use of WT-F2 is substantial. Although we could continue our compilation of basis sets along this line, we have decided to aim at higher accuracy than Clementi's for atoms beyond Zn ($Z=30$). The work is in progress.

Table 1
Total energy of He (^1S)

	7s	8s	9s	10s
GEOM.F	−2.861253923	−2.861507140	−2.861606310	−2.861647460
WT-F1	−2.861499558	−2.861616815	−2.861656716	−2.861671003
WT-F2	−2.861511566	−2.861623477	−2.861660042	−2.861672607
REF	−2.861514220	−2.861624827	−2.861660624	−2.861672938

Table 2
Optimized orbital exponents (10s) for He (^1S)

	GEOM.F	WT-F1	WT-F2	REF
ζ_{10}	1470.0088	4032.5699	4678.1257	4840.888547
ζ_9	533.42687	775.56618	764.76307	723.108918
ζ_8	193.56634	168.42435	166.81744	164.299706
ζ_7	70.240047	45.884678	46.060491	46.636262
ζ_6	25.488234	15.490807	15.097137	15.277787
ζ_5	9.2489983	5.8505319	5.5164495	5.526897
ζ_4	3.3562140	2.2918554	2.1381389	2.132879
ζ_3	1.2178803	0.90479794	0.85121324	0.849674
ζ_2	0.44193618	0.35754028	0.34216834	0.343643
ζ_1	0.16036682	0.14129171	0.13788429	0.138709

Table 3
Total energy and basis set size for He through Cd

	Atom	NUMER.HF	GEOM.F	s	p	d	WT-F2	s	p	d
2	He ^1S	2.81616800	2.861679919	20	0	0	2.861679975	17	0	0
3	Li ^2S	7.4327269	7.432726628	23	0	0	7.432726846	20	0	0
4	Be ^1S	14.573023	14.57302275	23	0	0	14.57302299	20	0	0
5	B ^2P	24.529061	24.52905991	23	16	0	24.52906021	20	13	0
6	C ^3P	37.688619	37.68861771	23	16	0	37.68861796	20	13	0
7	N ^4S	54.400934	54.40093197	23	16	0	54.40093246	20	13	0
8	O ^3P	74.809398	74.80939576	23	16	0	74.80939527	20	13	0
9	Fe ^2P	99.409349	99.40934542	23	16	0	99.40934426	20	13	0
10	Ne ^1S	128.54720	128.5470926	23	16	0	128.5470905	20	13	0
11	Na ^2S	161.85891	161.8588998	26	16	0	161.8589015	23	13	0
12	Mg ^1S	199.61463	199.6146191	26	16	0	199.6146236	23	13	0
13	Al ^2P	241.87671	241.8766983	26	20	0	241.8766931	23	16	0
14	Si ^3P	288.85436	288.8543509	26	20	0	288.8543469	23	16	0
15	P ^4S	340.71878	340.7187678	26	20	0	340.7187652	23	16	0
16	S ^3P	397.50490	397.5048754	26	20	0	397.5048764	23	16	0

Table 3 (continued)

17	Cl ^{2}P	459.48207	459.4820518	26	20	0	459.4820498	23	16	0
18	Ar ^{1}S	526.81751	526.8174840	26	20	0	526.8174873	23	16	0
19	K ^{2}S	599.16479	599.1647600	29	20	0	599.1647582	26	16	0
20	Ca ^{1}S	676.75818	676.7581414	29	20	0	676.7581540	26	16	0
21	Sc ^{2}D	759.73572	759.7356890	30	20	18	759.7356986	26	17	13
22	Ti ^{3}F	848.40600	848.4059695	30	21	17	848.4059758	26	17	13
23	V ^{4}F	942.88433	942.8843114	30	21	17	942.8843139	26	17	13
24	Cr ^{7}S	1043.357	1043.356355	30	21	17	1043.356337	26	17	13
25	Mn ^{6}S	1149.8662	1149.866208	30	21	17	1149.866220	26	17	13
26	Fe ^{5}D	1262.4437	1262.443611	30	21	17	1262.443628	26	17	13
27	Co ^{4}F	1381.4146	1381.414500	30	21	17	1381.414509	26	17	13
28	Ni ^{3}F	1506.8709	1506.870851	30	22	17	1506.870857	26	17	13
29	Cu ^{2}S	1638.965	1638.963683	30	20	17	1638.963687	26	17	14
30	Zn ^{1}S	1777.8481	177.848057	30	21	17	1777.848068	26	17	14
31	Ga ^{2}P	1923.2610	1923.260927	30	23	17	1923.260899	26	19	14
32	Ge ^{3}P	2075.3597	2075.359673	30	24	17	2075.359637	26	19	14
33	As ^{4}S	2234.2386	2234.238580	30	23	17	2234.238565	26	19	14
34	Se ^{3}P	2399.8676	2399.867531	30	24	17	2399.867518	26	19	14
35	Br ^{2}P	2572.4413	2572.441215	30	24	17	2572.441238	26	19	14
36	Kr ^{1}S	2752.0550	2752.054830	30	24	17	2752.054881	26	19	14
37	Rb ^{2}S	2938.3574	2938.357090	32	25	17	2938.357281	26	19	13
38	Sr ^{1}S	3131.5457	3131.544919	33	24	17	3131.545393	26	19	13
39	Y ^{2}D	3331.6842	3331.683006	33	24	20	3331.683849	26	19	16
40	Zr ^{5}F	3539.0096	3539.993279 [a]	33	24	20	3539.009325	26	19	16
41	Nb ^{6}D	3753.5977	3753.597436	33	24	20	3753.597475	26	19	17
42	Mo ^{7}S	3975.5495	3975.549276	32	24	20	3975.549246	26	19	16
43	Tc ^{6}S	4204.7887	4204.788515	32	24	20	4204.788537	26	19	16
44	Ru ^{5}F	4441.5395	4441.539167	32	24	20	4441.539209	26	19	16
45	Rh ^{4}F	4685.8817	4685.881433	32	24	20	4685.881416	26	19	16
46	Pd ^{1}S	4937.9210	4937.920781	30	24	20	4937.920745	26	19	16
47	Ag ^{2}S	5197.6985	5197.698193	32	24	20	5197.698159	26	19	16
48	Cd ^{1}S	5465.1331	5465.132700	33	24	20	5465.132866	26	19	16

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