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Double even tempering of orbital exponents: Application to Roothaan–Hartree–Fock calculations for He through Xe in Slater-type basis sets

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Summary. Double even tempering (DET) of orbital exponents is proposed as a useful generalization of even tempering (ET). The DET scheme uses two sets of basis functions for each angular momentum. The two sets have different principal quantum numbers and their exponents are generated by two different geometric sequences. Roothaan–Hartree–Fock (RHF) calculations on the atoms from He through Xe using both ET and DET Slater-type basis sets of the same size are carried out to demonstrate the substantial improvement offered by the DET scheme. The DET scheme reduces the maximum deviation of the RHF energies relative to the Hartree–Fock limit from 1.4 to 0.3 millihartrees.

Key words: Doubly even tempered wavefunctions – Slater-type basis functions – Atoms He through Xe

1 Introduction

Even tempering is a method for reducing the number of nonlinear parameters required to specify a basis set. The simplest realization of this idea arises in the construction of one-particle basis sets [1–8] for electronic structure calculations. For example, if an orbital basis set contains M_l Slater-type functions (STFs) corresponding to the angular momentum quantum number l, then the unnormalized radial parts of the STFs are taken to be $r^l \exp(-\zeta_{li} r)$ with the exponents in a geometric sequence $\zeta_{li} = \alpha_l \beta_l^i$ defined by the two nonlinear parameters α_l and β_l.

Two practical advantages of the even tempering procedure are immediately evident. The number of nonlinear parameters that need to be variationally optimized is reduced from M_l to 2 for each symmetry resulting in a substantial reduction of computational effort. Moreover, when the basis set needs to be extended with tighter functions for calculations of, say, the electric field gradient at the nucleus or more diffuse functions for polarizabilities, then the geometric sequence provides an unambiguous recipe for the choice of the added functions.

Even tempering also carries a penalty. It requires approximately one extra function of each symmetry to achieve an accuracy comparable to that of a fully optimized basis set [9, 10]. This shortcoming can be ameliorated by using more nonlinear parameters per symmetry. One such method is the well tempered (WT) scheme [11–14] where a more complex relationship, with four nonlinear parameters, is used to specify the orbital exponents.

We have recently suggested that two geometric sequences be used for each symmetry [10]. We shall refer to this idea as double even tempering. The purpose of this paper is to demonstrate the power of this scheme. This is achieved by comparing Roothaan–Hartree–Fock (RHF) energies for all atoms from He through Xe using fully optimized, even tempered (ET), and double even tempered (DET) STF basis sets of the same size. Most of the energy loss in the ET sets is recovered by the DET sets, and the DET wavefunctions are satisfactory approximations to the Hartree–Fock (HF) limit. Hartree atomic units are used throughout.

2 Double even tempering

The exponents of the radial functions in a double even tempered basis set are given by two independent geometric sequences for each angular momentum [10]. Thus,

$$\zeta_{li} = \begin{cases} \alpha_l \beta_l^i & \text{for} \quad i = 1, 2, \cdots, K_l, \\ \bar{\alpha}_l \bar{\beta}_l^{i-K_l} & \text{for} \quad i = K_l + 1, K_l + 2, \cdots, M_l. \end{cases} \tag{1}$$

The original even tempered scheme corresponds to using only the first geometric sequence with $K_l = M_l$. Equation (1) does not specify the DET scheme uniquely. Two more items need to be specified to obtain a unique prescription: the apportioning parameter K_l and the principal quantum numbers n of the basis functions generated by the two geometric series.

We assign the two sequences essentially equal weight by setting $K_l = \text{int}[(M_l \pm 1)/2]$ where int represents the integer part. Thus, if we have an even number of basis functions they are divided equally between the two series, and if we have an odd number the first series is assigned one function more or less than the second series.

We performed preliminary calculations [10] on the xenon atom to determine an appropriate method for assigning the principal quantum numbers n. One method is to use the same $n = l + 1$ quantum numbers for both series. In this case, the DET exponents simply form two different ET sequences. This allows for different distributions of small and large exponents. Another method is to let

$$n = \begin{cases} l + 1 & \text{for} \quad i = 1, 2, \cdots, K_l, \\ l + j & \text{for} \quad i = K_l + 1, K_l + 2, \cdots, M_l, \end{cases} \tag{2}$$

where $j = 2$ for STFs and $j = 3$ for Gaussian-type functions (GTFs). An odd j is necessary to preserve the simplicity of multicenter integrals for GTFs. Using two values of n for each l should reduce numerical linear dependence problems. DET calculations on Xe using $13s12p8d$ STFs gave an energy of -7232.1380 when the same $n = l + 1$ quantum numbers were used for both sequences, and an energy of -7232.1382 when Eq. (2) was used. By way of comparison, the WT scheme applied to a STF basis of the same size led to an energy of -7232.1380 for Xe. We expect Eq. (2) to be the more stable scheme in general and therefore adopted it.

Table 1. Deviations, in millihartrees, of the ET and DET energies from the numerical HF limits [15, 19] (listed in Hartrees with sign reversed)

Z	Atom	Present RHF			Numerical HF
		STFs	ET	DET	
2	He (^{1}S)	4*s*	0.0001	0.0001	2.8616800
3	Li (^{2}S)	7*s*	0.0010	0.0003	7.4327269
4	Be (^{1}S)	7*s*	0.002	0.000	14.573023
5	B (^{2}P)	7*s*5*p*	0.002	0.000	24.529061
6	C (^{3}P)	7*s*5*p*	0.004	0.000	37.688619
7	N (^{4}S)	7*s*5*p*	0.006	0.001	54.400934
8	O (^{3}P)	7*s*5*p*	0.008	0.001	74.809398
9	F (^{2}P)	7*s*5*p*	0.013	0.002	99.409349
10	Ne (^{1}S)	7*s*5*p*	0.02	0.01	128.54710
11	Na (^{2}S)	10*s*5*p*	0.04	0.00	161.85891
12	Mg (^{1}S)	10*s*5*p*	0.05	0.01	199.61464
13	Al (^{2}P)	10*s*8*p*	0.03	0.01	241.87671
14	Si (^{3}P)	10*s*8*p*	0.02	0.00	288.85436
15	P (^{4}S)	10*s*8*p*	0.03	0.01	340.71878
16	S (^{3}P)	10*s*8*p*	0.07	0.01	397.50490
17	Cl (^{2}P)	10*s*8*p*	0.06	0.01	459.48207
18	Ar (^{1}S)	10*s*8*p*	0.06	0.02	526.81751
19	K (^{2}S)	11*s*7*p*	0.15	0.06	599.16479
20	Ca (^{1}S)	11*s*7*p*	0.16	0.04	676.75819
21	Sc (^{2}D)	11*s*7*p*5*d*	0.17	0.04	759.73572
22	Ti (^{3}F)	11*s*7*p*5*d*	0.19	0.05	848.40600
23	V (^{4}F)	11*s*7*p*5*d*	0.21	0.06	942.88434
24	Cr (^{7}S)	11*s*7*p*5*d*	0.4	0.1	1043.3564
25	Mn (^{6}S)	11*s*7*p*5*d*	0.3	0.1	1149.8663
26	Fe (^{5}D)	11*s*7*p*5*d*	0.4	0.1	1262.4437
27	Co (^{4}F)	11*s*7*p*5*d*	0.5	0.1	1381.4146
28	Ni (^{3}F)	11*s*7*p*5*d*	0.6	0.1	1506.8709
29	Cu (^{2}S)	11*s*7*p*5*d*	0.8	0.1	1638.9637
30	Zn (^{1}S)	11*s*7*p*5*d*	0.6	0.1	1777.8481
31	Ga (^{2}P)	11*s*10*p*5*d*	0.5	0.1	1923.2610
32	Ge (^{3}P)	11*s*10*p*5*d*	0.4	0.0	2075.3597
33	As (^{4}S)	11*s*10*p*5*d*	0.5	0.1	2234.2387
34	Se (^{3}P)	11*s*10*p*5*d*	0.5	0.1	2399.8676
35	Br (^{2}P)	11*s*10*p*5*d*	0.6	0.0	2572.4413
36	Kr (^{1}S)	11*s*10*p*5*d*	0.7	0.1	2752.0550
37	Rb (^{2}S)	13*s*10*p*5*d*	0.8	0.2	2938.3575
38	Sr (^{1}S)	13*s*10*p*5*d*	0.6	0.2	3131.5457
39	Y (^{2}D)	13*s*10*p*8*d*	0.5	0.1	3331.6842
40	Zr (^{3}F)	13*s*10*p*8*d*	0.5	0.1	3538.9951
41	Nb (^{6}D)	13*s*10*p*8*d*	0.5	0.1	3753.5977
42	Mo (^{7}S)	13*s*10*p*8*d*	0.6	0.1	3975.5495
43	Tc (^{6}S)	13*s*10*p*8*d*	0.6	0.1	4204.7887
44	Ru (^{5}F)	13*s*10*p*8*d*	0.9	0.1	4441.5395
45	Rh (^{4}F)	13*s*10*p*8*d*	1.1	0.1	4685.8817
46	Pd (^{1}S)	13*s*10*p*8*d*	0.6	0.1	4937.9210
47	Ag (^{2}S)	13*s*10*p*8*d*	1.4	0.2	5197.6985
48	Cd (^{1}S)	13*s*10*p*8*d*	1.1	0.1	5465.1331
49	In (^{2}P)	13*s*12*p*8*d*	1.1	0.3	5740.1692
50	Sn (^{3}P)	13*s*12*p*8*d*	0.8	0.2	6022.9317
51	Sb (^{4}S)	13*s*12*p*8*d*	0.7	0.3	6313.4854
52	Te (^{3}P)	13*s*12*p*8*d*	0.7	0.3	6611.7841
53	I (^{2}P)	13*s*12*p*8*d*	0.6	0.2	6917.9809
54	Xe (^{1}S)	13*s*12*p*8*d*	0.6	0.2	7232.1384

Table 2. Parameters of the even-tempered wavefunctions. The number of STFs and the tempering parameters are shown for each atom

Z	Atom	1s			2p			3d		
		STFs	α	β	STFs	α	β	STFs	α	β
2	He (^{1}S)	4	0.853931	1.660897						
3	Li (^{2}S)	7	0.345201	1.629013						
4	Be (^{1}S)	7	0.445689	1.668493						
5	B (^{2}P)	7	0.581288	1.665156	5	0.552688	1.608452			
6	C (^{3}P)	7	0.705082	1.669878	5	0.671226	1.617303			
7	N (^{4}S)	7	0.824096	1.675504	5	0.780901	1.628541			
8	O (^{3}P)	7	0.948453	1.677177	5	0.814568	1.678221			
9	F (^{2}P)	7	1.068944	1.679954	5	0.874133	1.709478			
10	Ne (^{1}S)	7	1.187022	1.683000	5	0.945942	1.730277			
11	Na (^{2}S)	10	0.325220	1.644321	5	1.317132	1.650091			
12	Mg (^{1}S)	10	0.409381	1.612599	5	0.921399	1.811172			
13	Al (^{2}P)	10	0.527799	1.574138	8	0.412654	1.709027			
14	Si (^{3}P)	10	0.630704	1.552240	8	0.521586	1.665916			
15	P (^{4}S)	10	0.727880	1.537258	8	0.618595	1.646136			
16	S (^{3}P)	10	0.820373	1.526730	8	0.642315	1.680945			
17	Cl (^{2}P)	10	1.000253	1.411522	8	0.797830	1.461041			
18	Ar (^{1}S)	10	1.099655	1.404911	8	0.875358	1.456449			
19	K (^{2}S)	11	0.322860	1.498530	7	1.103242	1.452497			
20	Ca (^{1}S)	11	0.385183	1.479596	7	1.288802	1.430768			
21	Sc (^{2}D)	11	0.405090	1.479987	7	1.383761	1.426314	5	0.651504	1.815745
22	Ti (^{3}F)	11	0.420420	1.481960	7	1.477400	1.423204	5	0.756204	1.782576
23	V (^{4}F)	11	0.434908	1.483990	7	1.569113	1.420983	5	0.820930	1.779068
24	Cr (^{7}S)	11	0.439244	1.489215	7	1.562955	1.433423	5	0.663143	1.906257
25	Mn (^{6}S)	11	0.461452	1.488181	7	1.747304	1.418486	5	0.930974	1.783557
26	Fe (^{5}D)	11	0.476549	1.489389	7	1.829350	1.418423	5	0.933319	1.813631
27	Co (^{4}F)	11	0.490253	1.490881	7	1.911188	1.418585	5	0.956658	1.830643
28	Ni (^{3}F)	11	0.503317	1.492413	7	1.992054	1.418990	5	0.984353	1.843832

29	Cu (^{2}S)	11	0.482904	1.458094	7	1.972417	1.432099	5	0.526252	1.863712
30	Zn (^{1}S)	11	0.533550	1.449484	7	2.151532	1.420286	5	0.602339	1.837883
31	Ga (^{2}P)	11	0.633197	1.431852	10	0.488979	1.503318	5	1.305895	1.788412
32	Ge (^{3}P)	11	0.725878	1.418649	10	0.581983	1.478126	5	1.552925	1.735692
33	As (^{4}S)	11	0.816500	1.407808	10	0.671821	1.458876	5	1.790550	1.695311
34	Se (^{3}P)	11	0.898657	1.399592	10	0.709228	1.455727	5	2.029878	1.658888
35	Br (^{2}P)	11	0.980206	1.392420	10	0.766792	1.448119	5	2.259270	1.624161
36	Kr (^{1}S)	11	1.061633	1.386042	10	0.833000	1.439473	5	2.475762	1.575997
37	Rb (^{2}S)	13	0.346183	1.474949	10	1.009937	1.411427	5	1.935388	1.692219
38	Sr (^{1}S)	13	0.395344	1.462240	10	0.933071	1.431049	5	2.101756	1.663517
39	Y (^{2}D)	13	0.420801	1.457880	10	1.026499	1.419988	8	0.529324	1.653666
40	Zr (^{3}F)	13	0.437470	1.456293	10	1.100816	1.413214	8	0.583804	1.636927
41	Nb (^{6}D)	13	0.465178	1.451913	10	1.181932	1.405736	8	0.643077	1.620167
42	Mo (^{7}S)	13	0.478243	1.451510	10	1.266884	1.398749	8	0.717245	1.597084
43	Tc (^{6}S)	13	0.475356	1.455052	10	1.326261	1.396065	8	0.908435	1.513825
44	Ru (^{5}F)	13	0.487143	1.454807	10	1.407139	1.390534	8	0.823694	1.573468
45	Rh (^{4}F)	13	0.490616	1.456545	10	1.481768	1.386425	8	0.882368	1.559080
46	Pd (^{1}S)	13	1.778062	1.339474	10	1.514253	1.387661	8	0.704117	1.534805
47	Ag (^{2}S)	13	0.497055	1.459893	10	1.637339	1.378602	8	0.937901	1.487797
48	Cd (^{1}S)	13	0.530291	1.454746	10	1.714553	1.375400	8	1.155971	1.491450
49	In (^{2}P)	13	0.609498	1.440810	12	0.514895	1.456939	8	1.310075	1.465200
50	Sn (^{3}P)	13	0.677250	1.430673	12	0.596339	1.440002	8	1.434274	1.451809
51	Sb (^{4}S)	13	0.740782	1.422308	12	0.672910	1.426893	8	1.540856	1.444387
52	Te (^{3}P)	13	0.798602	1.415615	12	0.704534	1.423652	8	1.641257	1.439028
53	I (^{2}P)	13	0.854821	1.409715	12	0.753015	1.417766	8	1.733353	1.435778
54	Xe (^{1}S)	13	0.911055	1.404298	12	0.808964	1.411310	8	1.820593	1.433330

Table 3. Parameters of the doubly even-tempered wavefunctions. For each atom, the first line shows the number of STFs and the tempering parameters for 1*s*, 2*p*, and 3*d*, and the second line shows those for 2*s*, 3*p*, and 4*d*

Z	Atom	1s/2s			2p/3p			3d/4d		
		STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
2	He (^{1}S)	2	0.838997	2.235436						
		2	0.567170	2.715026						
3	Li (^{2}S)	3	0.201223	2.754677						
		4	0.297461	2.221885						
4	Be (^{1}S)	3	0.269896	2.752445						
		4	0.397285	2.238930						
5	B (^{2}P)	4	0.444482	2.181367	3	0.498820	2.265164			
		3	1.084840	2.324550	2	0.391023	2.342989			
6	C (^{3}P)	4	0.547713	2.168485	3	0.618294	2.260144			
		3	1.279669	2.340137	2	0.471184	2.360569			
7	N (^{4}S)	4	0.646363	2.160156	3	0.721102	2.269130			
		3	1.531871	2.224782	2	0.547338	2.359939			
8	O (^{3}P)	4	0.753356	2.127735	3	0.728332	2.361853			
		3	1.685721	2.145690	2	0.572575	2.371659			
9	F (^{2}P)	4	0.881716	2.037851	3	0.850628	2.339424			
		3	1.685446	2.185415	2	0.635951	2.409075			
10	Ne (^{1}S)	4	0.997985	1.990896	3	0.963963	2.344752			
		3	1.713280	2.249577	2	0.692635	2.463367			
11	Na (^{2}S)	5	0.525628	2.128889	3	0.434748	2.859692			
		5	0.255850	2.453826	2	0.853406	3.017753			
12	Mg (^{1}S)	5	0.616367	2.099007	3	0.535737	2.770420			
		5	0.321485	2.398906	2	1.087917	2.843641			
13	Al (^{2}P)	5	0.331828	2.495270	4	0.467640	2.320692			
		5	0.226302	2.634095	4	0.335399	2.370336			
14	Si (^{3}P)	5	0.619292	1.804947	4	0.541250	2.278270			
		5	0.544805	2.001513	4	0.416707	2.287103			
15	P (^{4}S)	5	0.740546	1.774720	4	0.560992	2.289565			

		5	0.632314	1.973730	4	0.470888	2.252622			
16	S (^{3}P)	5	1.104819	1.655977	4	0.603784	2.303992			
		5	0.734512	1.940722	4	0.504179	2.271607			
17	Cl (^{2}P)	5	1.165507	1.666337	4	0.632592	2.308057			
		5	0.809323	1.932401	4	0.539737	2.269498			
18	Ar (^{1}S)	5	1.164877	1.694865	4	0.671623	2.290215			
		5	0.874110	1.931334	4	0.581532	2.252524			
19	K (^{2}S)	6	0.485082	2.000847	4	0.423241	2.568394			
		5	0.229805	2.372677	3	0.762203	2.704226			
20	Ca (^{1}S)	6	0.553049	1.960663	4	0.426994	2.636164			
		5	0.282771	2.292085	3	0.876265	2.669519			
21	Sc (^{2}D)	6	0.578299	1.974600	4	0.478950	2.593999	3	0.395798	2.842157
		5	0.294765	2.305920	3	0.962061	2.639061	2	0.759711	2.931126
22	Ti (^{3}F)	6	0.597810	1.994871	4	0.556665	2.517206	3	0.464047	2.753630
		5	0.301818	2.329700	3	1.060467	2.593128	2	0.871878	2.843395
23	V (^{4}F)	6	0.616390	2.013907	4	0.643489	2.444905	3	0.506764	2.719114
		5	0.307654	2.354600	3	1.164635	2.549116	2	0.941441	2.814500
24	Cr (^{7}S)	6	0.267775	2.186795	4	0.908284	2.222019	3	0.402298	2.921641
		5	0.752099	2.032059	3	1.431557	2.379155	2	0.754811	3.089189
25	Mn (^{6}S)	6	0.293760	2.161983	4	0.897435	2.269691	3	0.576125	2.682924
		5	0.821580	2.007175	3	1.444217	2.427358	2	1.048055	2.801409
26	Fe (^{5}D)	6	0.300878	2.168805	4	1.003447	2.226728	3	0.575073	2.710382
		5	0.848801	2.011879	3	1.581529	2.390480	2	1.039522	2.853943
27	Co (^{4}F)	6	0.306813	2.176965	4	1.085170	2.207001	3	0.586792	2.718966
		5	0.873073	2.017929	3	1.696716	2.373438	2	1.050532	2.885265
28	Ni (^{3}F)	6	0.312259	2.185535	4	1.156986	2.195859	3	0.601903	2.722440
		5	0.895149	2.024814	3	1.803310	2.363531	2	1.067126	2.909724
29	Cu (^{2}S)	6	0.947925	1.970310	4	1.189212	2.210151	3	0.505526	2.858931
		5	0.302490	2.549492	3	1.885912	2.369901	2	0.894305	2.120455
30	Zn (^{1}S)	6	0.321927	2.201807	4	1.279268	2.188754	3	0.643237	2.713728
		5	0.932911	2.039086	3	1.993175	2.358757	2	1.119471	2.933952
31	Ga (^{2}P)	6	0.407384	2.123666	5	0.506939	2.298520	3	0.790313	2.595404
		5	1.113756	1.976472	5	0.332643	2.436715	2	1.350622	2.789893
32	Ge (^{3}P)	6	0.479608	2.074871	5	0.655285	2.179016	3	0.918988	2.514996
		5	1.258019	1.938663	5	0.419192	2.330193	2	1.554730	2.689603

Table 3. (Continued)

Z	Atom	$1s/2s$			$2p/3p$			$3d/4d$		
		STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
33	As (^{4}S)	6	0.547094	2.037066	5	0.783315	2.108459	3	1.007470	2.475908
		5	1.394060	1.907868	5	0.496739	2.264367	2	1.698097	2.641822
34	Se (^{3}P)	6	0.610416	2.010319	5	0.814390	2.111119	3	1.044832	2.470363
		5	1.506983	1.890084	5	0.524433	2.261090	2	1.776293	2.626519
35	Br (^{2}P)	6	0.666638	1.989354	5	1.126036	1.952725	3	1.083893	2.464036
		5	1.538959	1.892348	5	0.587917	2.198730	2	1.868985	2.602018
36	Kr (^{1}S)	6	0.734557	1.960283	5	1.232375	1.926692	3	1.073002	2.488579
		5	1.746261	1.848324	5	0.639230	2.175650	2	1.887080	2.615180
37	Rb (^{2}S)	7	0.192199	2.173035	5	1.352552	1.821582	3	1.124639	2.474955
		6	0.529113	2.054960	5	0.805331	1.949498	2	1.976428	2.599892
38	Sr (^{1}S)	7	0.248276	2.121308	5	1.337081	1.834413	3	1.161848	2.470899
		6	0.657141	2.007537	5	0.914668	1.909865	2	2.039050	2.599967
39	Y (^{2}D)	7	0.257436	2.121988	5	1.364491	1.833646	4	0.619864	2.335535
		6	0.682440	2.007340	5	0.939289	1.906194	4	0.439043	2.405498
40	Zr (^{3}F)	7	0.268006	2.113365	5	1.462577	1.825137	4	0.667439	2.319525
		6	0.709817	1.999312	5	0.995099	1.903101	4	0.486178	2.373948
41	Nb (^{6}D)	7	0.274096	2.111115	5	1.611951	1.801454	4	0.709355	2.297554
		6	0.726951	1.997189	5	1.053925	1.894121	4	0.493783	2.383498
42	Mo (^{7}S)	7	0.280813	2.111254	5	1.652220	1.803522	4	0.724320	2.305839
		6	0.743840	1.997856	5	1.129784	1.879936	4	0.523786	2.368899
43	Tc (^{6}S)	7	0.288134	2.115136	5	1.699113	1.804349	4	0.740012	2.308988
		6	0.775902	1.995778	5	1.180912	1.875164	4	0.544493	2.362411
44	Ru (^{5}F)	7	0.279970	2.084561	5	1.942678	1.767738	4	0.765899	2.304402
		6	0.834583	1.932268	5	1.243373	1.868434	4	0.549003	2.375767

45	Rh (^{4}F)	7	0.287183	2.088192	5	2.004860	1.767370	4	0.809256	2.292627
		6	0.860936	1.935891	5	1.286115	1.867856	4	0.577834	2.368323
46	Pd (^{1}S)	7	1.088597	1.729286	5	1.971073	1.785851	4	0.771217	2.345587
		6	1.935581	1.689871	5	1.289047	1.881078	4	0.522657	2.452920
47	Ag (^{2}S)	7	0.283285	2.090043	5	2.070025	1.775387	4	0.931385	2.241688
		6	0.739967	1.973661	5	1.400863	1.857156	4	0.656613	2.330114
48	Cd (^{1}S)	7	0.324958	2.057522	5	2.157408	1.770928	4	0.983741	2.246702
		6	0.846871	1.941083	5	1.477089	1.848646	4	0.712608	2.319764
49	In (^{2}P)	7	0.386679	2.065618	6	0.638233	1.928444	4	1.088080	2.205606
		6	1.012085	1.951698	6	0.373491	2.047700	4	0.789332	2.280807
50	Sn (^{3}P)	7	0.447083	2.031309	6	0.672903	1.918912	4	1.234157	2.148160
		6	1.135184	1.923427	6	0.446700	1.995699	4	0.898166	2.224557
51	Sb (^{4}S)	7	0.503351	2.002684	6	0.693246	1.916069	4	1.305634	2.133344
		6	1.248401	1.899558	6	0.511723	1.958225	4	0.939398	2.218442
52	Te (^{3}P)	7	0.557410	1.978986	6	0.722696	1.910039	4	1.252896	2.172313
		6	1.355911	1.879692	6	0.537452	1.950033	4	0.878880	2.273432
53	I (^{2}P)	7	0.609349	1.957802	6	0.739978	1.909187	4	1.269183	2.176300
		6	1.458308	1.861806	6	0.572892	1.936508	4	0.891512	2.277297
54	Xe (^{1}S)	7	0.658448	1.942397	6	0.752945	1.911092	4	1.286042	2.186275
		6	1.556669	1.848450	6	0.607254	1.925597	4	0.917964	2.277813

More complicated choices of n could be made but the simplicity of Eq. (2) appeals to us.

We examined the DET scheme defined by Eqs. (1) and (2) by performing RHF calculations on the ground states of all atoms from He through Xe. We choose STF basis sets of precisely the same size as those used by Bunge et al. [15] who were able to effectively reach the HF limit by complete optimization of the exponents and partial optimization of the principal quantum numbers. We also constructed conventional ET wavefunctions in STF basis sets of the same size for the purposes of comparison.

All calculations were carried out using our corrected and modified version [16] of Pitzer's program [17]. The tempering parameters were variationally optimized using the method of conjugate directions [18]. In all cases, the optimization was sufficiently thorough to ensure that the virial ratio was $-2 \pm 1 \times 10^{-7}$.

3 Results and discussion

Table 1 lists the deviations of our ET and DET energies from the HF limit, and the RHF energies obtained by Bunge et al. [15] using fully optimized STF basis sets of the same size. Their RHF energies coincide with numerical HF energies [15, 19] to the number of figures listed. Table 1 shows that the ET energies do not differ from the HF limits by more than 0.02, 0.07, 0.8, and 1.4 millihartrees, respectively, for first-, second-, third-, and fourth-row atoms. The ET energies are similar to, or lower than, the benchmark results obtained by Clementi and Roetti [20] with slightly smaller but fully optimized basis sets. Our results are testimony to the effectiveness of the ET method despite its limited variational freedom. For example, in Xe the ET method reduces the optimization problem from 33 STF exponents to just 6 nonlinear parameters. The tempering parameters are listed in Table 2.

The ET method is weakest for atoms which contain both very tight and diffuse atomic orbitals (AOs) of the same symmetry. For example, the largest deviation from the HF limit is found in Ag where there is a very tight 1*s* AO and a very diffuse 5*s* AO. It appears that a single geometric series does not generate an *s*-basis flexible enough to describe accurately both these AOs.

The DET method improves the results for such atoms very markedly, as shown in Table 1. The DET energies are within 0.01, 0.02, 0.1, and 0.3 millihartrees, respectively, of the HF limits for the first-, second-, third-, and fourth-row atoms. All the DET orbital energies were found to be very close to the HF limit values [19]. The DET wavefunctions are, in our opinion, excellent analytical approximations to the HF wavefunctions. The tempering parameters are listed in Table 3.

The success of the DET scheme is due to its increased variational flexibility relative to the ET scheme. The use of two sequences of exponents permits an optimal distribution of both small and large exponents. The use of two principal quantum numbers increases the numerical linear independence of the basis set. The increased flexibility comes at the expense of doubling the number of nonlinear parameters relative to the original ET method. Even so, the DET scheme is computationally far less demanding than full optimization for heavier atoms.

The WT scheme [11–14] has 4 nonlinear parameters just as the DET scheme does. Since the WT exponent formula depends explicitly on M_l, the number of basis functions in the symmetry l, it is not clear how to extend the original basis set to include more diffuse or tight functions when required. The ET and DET schemes do not share this M_l dependence, allowing an ET or DET basis to be augmented by extra diffuse or tight functions more easily. We also note that the WT scheme was designed mainly to improve the distribution of larger exponents in GTF basis sets. An application of the DET scheme to Gaussian basis sets would be interesting.

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