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Roothaan–Hartree–Fock wave functions for cations and anions in Slater-type basis sets with doubly even tempered exponents

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Summary. Roothaan–Hartree–Fock wave functions in Slater-type basis sets are reported for the cations Li^+–Cs^+ and anions H^-–I^- using the double even tempering (DET) method of selecting orbital exponents. The DET total energies do not differ from the corresponding numerical Hartree–Fock values by more than 0.2 millihartrees for the cations and anions. The present results together with the previous ones for neutral atoms [Theor Chim Acta 88:273 (1994)] provide a compilation of DET wave functions of near Hartree–Fock quality for all the neutral and singly-charged atoms with the number of electrons $N \leqslant 54$.

Key words: Doubly even tempered wave functions – Slater-type basis functions – Cations Li^+ through Cs^+ – Anions H^- through I^-

The even tempering (ET) method [1–8] specifies the orbital exponents of a basis set using sets of two nonlinear parameters α_l and β_l. In the case of Slater-type functions (STFs), the unnormalized radial parts of the STFs are taken to be $r^l \exp(-\zeta_{li} r)$ for the symmetry with angular momentum quantum number l, and the exponents are defined by a geometric sequence $\zeta_{li} = \alpha_l \beta_l^i$. Practical advantages of the ET method are (i) drastic reduction of the number of nonlinear parameters needed to specify a basis set, and (ii) facile extension of ET basis sets when additional diffuse or tight functions are required. On the other hand, the ET method has the disadvantage [9–11] that it requires approximately one extra basis function, for each symmetry, to achieve an accuracy comparable to that of a basis set with fully optimized exponents.

To reduce this disadvantage, while preserving the advantages of the ET scheme, we have recently proposed [10, 11] a double even tempering (DET) scheme which uses two independent geometric sequences for the exponents of each symmetry. In the case of STF basis sets, we also suggested the use of STFs with the lowest two principal quantum numbers for the two geometric sequences. Namely, the unnormalized radial functions for the symmetry l are given by $r^l \exp(-\zeta_{li} r)$ with $\zeta_{li} = \alpha_l \beta_l^i$ and $r^{l+1} \exp(-\bar{\zeta}_{li} r)$ with $\bar{\zeta}_{li} = \bar{\alpha}_l \bar{\beta}_l^i$. For simplicity we assign the two series the same number of functions if we have an even number of basis functions. If we have an odd number, the first series is assigned one function more or less than

Table 1. Energetic effect of parameter optimizations and increases in basis size for C and Se atoms. Subscript n means calculations with neutral exponents and opt means calculations with exponents optimized for respective ions. Prime (′) means calculations with one more primitive per symmetry than the basis sets specified in the heading

	Energy differences from NHF in millihartrees					
	Carbon (7s5p)			Selenium (11s10p5d)		
	$C(^3P)$	$C^+(^2P)$	$C^-(^4S)$	$Se(^3P)$	$Se^+(^4S)$	$Se^-(^2P)$
ET_n	0.00370	1.53012	10.47270	0.562	0.625	4.152
ET_{opt}	0.00370	0.00451	0.01364	0.562	0.380	0.982
ET'_{opt}	0.00009	0.00011	0.00199	0.136	0.061	0.223
DET_n	0.00022	3.32711	6.31304	0.069	1.354	6.236
DET_{opt}	0.00022	0.00032	0.00788	0.069	0.061	0.169
DET'_{opt}	0.00003	0.00003	0.00042	0.040	0.028	0.082

the second. We have applied [11] the DET method to Roothaan–Hartree–Fock (RHF) calculations of neutral atoms from He to Xe, and demonstrated the substantial improvement offered by the DET scheme: Compared to the ET method, the DET method reduces the maximum deviation of the RHF energies relative to the numerical Hartree–Fock (NHF) values from 1.4 to 0.3 millihartrees for the neutral atoms.

In the present paper, we report DET RHF wave functions for cations Li^+–Cs^+ and anions H^-–I^- in their ground states. We have also constructed conventional ET wave functions in STF basis sets of the same size for comparison. All the present calculations were carried out using the corrected and modified version [12] of Pitzer's program [13]. The tempering parameters were variationally optimized using the method of conjugate directions [14]. Reference NHF computations were performed by using a version [15] of MCHF72 [16] modified to improve the numerical accuracy.

Table 1 compares RHF energies for C, C^+ and C^- using ET and DET basis sets optimized for C with RHF energies using ET and DET basis sets of the same size optimized separately for C, C^+ and C^-. Similar comparisons are also tabulated for Se and its ions. The table shows clearly that using neutral atom basis sets for ions raises the energy error relative to the NHF limits substantially. This effect is more pronounced for the anion than for the cation, and greater in carbon than in selenium. Separate optimization of the ET and DET basis sets in each of the species leads to RHF energies of comparable accuracy for the neutral atom and the cation, but the RHF energies for the anions are still worse by factors ranging from 2 to 30. This is because the basis sets need more flexibility to describe the diffuse character of orbitals due to the additional electron. Table 1 shows that RHF energies of comparable accuracy for the neutral, cation and anion can be obtained by using separately optimized basis sets and using one extra basis function of each symmetry for the anion. Hence, in the rest of this work, we use cation basis sets of exactly the same size as used previously for a neutral atom with N electrons [11], whereas the size of a basis set for an N-electron anion is that for an N-electron neutral atom augmented by one STF for *each* symmetry.

Table 2 summarizes the deviations of our ET and DET total energies from the NHF values for the cations Li^+–Cs^+ in their ground states [17]. From Table 1, we

Table 2. Deviations (in millihartrees) of the ET and DET energies from the numerical HF values (in hartrees with sign reversed) for the cations Li^+ through Cs^+

Z	Cation	Configuration	State	NHF	RHF		
					STFs	ET	DET
3	Li^+	1s(2)	1S	7.236415201	4s	0.000080	0.000037
4	Be^+	...2s(1)	2S	14.27739481	7s	0.00108	0.00017
5	B^+	...2s(2)	1S	24.23757518	7s	0.00223	0.00012
6	C^+	...2s(2)2p(1)	2P	37.29222377	7s5p	0.00451	0.00032
7	N^+	...2s(2)2p(2)	3P	53.88800501	7s5p	0.00575	0.00055
8	O^+	...2s(2)2p(3)	4S	74.37260568	7s5p	0.00779	0.00061
9	F^+	...2s(2)2p(4)	3P	98.83172020	7s5p	0.00972	0.00068
10	Ne^+	...2s(2)2p(5)	2P	127.8178141	7s5p	0.0128	0.0007
11	Na^+	...2s(2)2p(6)	1S	161.6769626	7s5p	0.0174	0.0016
12	Mg^+	...3s(1)	2S	199.3718097	10s5p	0.0482	0.0043
13	Al^+	...3s(2)	1S	241.6746705	10s5p	0.0380	0.0054
14	Si^+	...3s(2)3p(1)	2P	288.5731311	10s8p	0.0117	0.0051
15	P^+	...3s(2)3p(2)	3P	340.3497759	10s8p	0.0140	0.0058
16	S^+	...3s(2)3p(3)	4S	397.1731828	10s8p	0.0166	0.0068
17	Cl^+	...3s(2)3p(4)	3P	459.0485907	10s8p	0.0294	0.0090
18	Ar^+	...3s(2)3p(5)	2P	526.2745343	10s8p	0.0507	0.0123
19	K^+	...3s(2)3p(6)	1S	599.0175794	10s8p	0.0810	0.0162
20	Ca^+	...4s(1)	2S	676.5700126	11s7p	0.1342	0.0676
21	Sc^+	...4s(1)3d(1)	3D	759.5391440	11s7p5d	0.1337	0.0720
22	Ti^+	...4s(1)3d(2)	4F	848.2034008	11s7p5d	0.1345	0.0745
23	V^+	...4s(0)3d(4)	5D	942.6707837	11s7p5d	0.1064	0.0396
24	Cr^+	...4s(0)3d(5)	6S	1043.139393	11s7p5d	0.113	0.039
25	Mn^+	...4s(1)3d(5)	7S	1149.649383	11s7p5d	0.146	0.071
26	Fe^+	...4s(1)3d(6)	6D	1262.213012	11s7p5d	0.158	0.071
27	Co^+	...4s(0)3d(8)	3F	1381.128750	11s7p5d	0.267	0.043
28	Ni^+	...4s(0)3d(9)	2D	1506.591099	11s7p5d	0.398	0.048
29	Cu^+	...4s(0)3d(10)	1S	1638.728242	11s7p5d	0.471	0.056
30	Zn^+	...4s(1)3d(10)	2S	1777.567545	11s7p5d	0.341	0.084

Table 2. (Continued)

Z	Cation	Configuration	State	NHF	RHF		
					STFs	ET	DET
31	Ga^+	...4s(2)3d(10)	1S	1923.059722	11s7p5d	0.280	0.083
32	Ge^+	...4s(2)4p(1)	2P	2075.086491	11s10p5d	0.268	0.065
33	As^+	...4s(2)4p(2)	3P	2233.888335	11s10p5d	0.316	0.063
34	Se^+	...4s(2)4p(3)	4S	2399.558574	11s10p5d	0.380	0.061
35	Br^+	...4s(2)4p(4)	3P	2572.045211	11s10p5d	0.461	0.065
36	Kr^+	...4s(2)4p(5)	2P	2751.567394	11s10p5d	0.530	0.071
37	Rb^+	...4s(2)4p(6)	1S	2938.219931	11s10p5d	0.529	0.062
38	Sr^+	...5s(1)	2S	3131.373777	13s10p5d	0.351	0.089
39	Y^+	...5s(2)	1S	3331.472882	13s10p5d	0.314	0.085
40	Zr^+	...5s(1)4d(2)	4F	3538.809305	13s10p8d	0.355	0.077
41	Nb^+	...5s(0)4d(4)	5D	3753.389513	13s10p8d	0.302	0.042
42	Mo^+	...5s(0)4d(5)	6S	3975.333703	13s10p8d	0.297	0.041
43	Tc^+	...5s(1)4d(5)	7S	4204.594360	13s10p8d	0.348	0.079
44	Ru^+	...5s(0)4d(7)	4F	4441.321956	13s10p8d	0.304	0.045
45	Rh^+	...5s(0)4d(8)	3F	4685.664172	13s10p8d	0.321	0.049
46	Pd^+	...5s(0)4d(9)	2D	4937.675930	13s10p8d	0.349	0.052
47	Ag^+	...5s(0)4d(10)	1S	5197.481334	13s10p8d	0.385	0.058
48	Cd^+	...5s(1)4d(10)	2S	5464.878609	13s10p8d	0.499	0.133
49	In^+	...5s(2)4d(10)	1S	5739.978392	13s10p8d	0.455	0.141
50	Sn^+	...5s(2)5p(1)	2P	6022.678323	13s12p8d	0.445	0.221
51	Sb^+	...5s(2)5p(2)	3P	6313.165941	13s12p8d	0.395	0.217
52	Te^+	...5s(2)5p(3)	4S	6611.503394	13s12p8d	0.361	0.214
53	I^+	...5s(2)5p(4)	3P	6917.627273	13s12p8d	0.357	0.217
54	Xe^+	...5s(2)5p(5)	2P	7231.708947	13s12p8d	0.352	0.205
55	Cs^+	...5s(2)5p(6)	1S	7553.810329	13s12p8d	0.351	0.191

Table 3. Deviations (in millihartrees) of the ET and DET energies from the numerical HF values (in hartrees with sign reversed) for the anions H^- through I^-

Z	Anion	Configuration	State	NHF	RHF		
					STFs	ET	DET
1	H^-	1s(2)	1S	0.4879297344	5s	0.0001171	0.0000287
3	Li^-	...2s(2)	1S	7.428232061	8s	0.001214	0.000651
5	B^-	...2s(2)2p(2)	3P	24.51922137	8s6p	0.00149	0.00062
6	C^-	...2s(2)2p(3)	4S	37.70884362	8s6p	0.00199	0.00042
7	N^-	...2s(2)2p(4)	3P	54.32195889	8s6p	0.00253	0.00080
8	O^-	...2s(2)2p(5)	2P	74.78974593	8s6p	0.00378	0.00077
9	F^-	...2s(2)2p(6)	1S	99.45945391	8s6p	0.00493	0.00082
11	Na^-	...3s(2)	1S	161.8551260	11s6p	0.0185	0.0076
13	Al^-	...3s(2)3p(2)	3P	241.8782653	11s9p	0.0160	0.0055
14	Si^-	...3s(2)3p(3)	4S	288.8896602	11s9p	0.0238	0.0052
15	P^-	...3s(2)3p(4)	3P	340.6988736	11s9p	0.0386	0.0060
16	S^-	...3s(2)3p(5)	2P	397.5384302	11s9p	0.0578	0.0069
17	Cl^-	...3s(2)3p(6)	1S	459.5769253	11s9p	0.0581	0.0066
19	K^-	...4s(2)	1S	599.1619170	12s8p	0.2473	0.0513
21	Sc^-	...4s(2)3d(2)	3F	759.6887738	12s8p6d	0.2779	0.0536
22	Ti^-	...4s(2)3d(3)	4F	848.3725498	12s8p6d	0.3337	0.0580
23	V^-	...4s(2)3d(4)	5D	942.8631322	12s8p6d	0.3621	0.0652
24	Cr^-	...4s(2)3d(5)	6S	1043.337097	12s8p6d	0.403	0.074
25	Mn^-	...4s(2)3d(6)	5D	1149.729110	12s8p6d	0.441	0.082
26	Fe^-	...4s(2)3d(7)	4F	1262.367074	12s8p6d	0.494	0.091
27	Co^-	...4s(2)3d(8)	3F	1381.351810	12s8p6d	0.560	0.102
28	Ni^-	...4s(2)3d(9)	2D	1506.821133	12s8p6d	0.640	0.112
29	Cu^-	...4s(2)3d(10)	1S	1638.964145	12s8p6d	0.737	0.123
31	Ga^-	...4s(2)4p(2)	3P	1923.260381	12s11p6d	0.487	0.145
32	Ge^-	...4s(2)4p(3)	4S	2075.394742	12s11p6d	0.256	0.108
33	As^-	...4s(2)4p(4)	3P	2234.222940	12s11p6d	0.236	0.094
34	Se^-	...4s(2)4p(5)	2P	2399.904726	12s11p6d	0.223	0.082
35	Br^-	...4s(2)4p(6)	1S	2572.536273	12s11p6d	0.224	0.067

Table 3. (Continued)

Z	Anion	Configuration	State	NHF	RHF		
					STFs	ET	DET
37	Rb^-	... 5s(2)	1S	2938.354900	14s11p6d	1.142	0.094
39	Y^-	... 5s(2)4d(1)5p(1)	1D	3331.683116	14s13p9d	0.510	0.146
40	Zr^-	... 5s(2)4d(3)	4F	3538.994500	14s11p9d	0.957	0.071
41	Nb^-	... 5s(2)4d(4)	5D	3753.578216	14s11p9d	1.104	0.067
42	Mo^-	... 5s(2)4d(5)	6S	3975.526268	14s11p9d	1.288	0.065
43	Tc^-	... 5s(2)4d(6)	5D	4204.764631	14s11p9d	1.357	0.064
44	Ru^-	... 5s(2)4d(7)	4F	4441.528477	14s11p9d	1.463	0.067
45	Rh^-	... 5s(2)4d(8)	3F	4685.875582	14s11p9d	1.585	0.075
46	Pd^-	... 5s(2)4d(9)	2D	4937.891544	14s11p9d	1.721	0.088
47	Ag^-	... 5s(2)4d(10)	1S	5197.700050	14s11p9d	1.880	0.102
49	In^-	... 5s(2)5p(2)	3P	5740.175141	14s13p9d	0.927	0.242
50	Sn^-	... 5s(2)5p(3)	4S	6022.972657	14s13p9d	0.593	0.169
51	Sb^-	... 5s(2)5p(4)	3P	6313.481518	14s13p9d	0.544	0.151
52	Te^-	... 5s(2)5p(5)	2P	6611.827949	14s13p9d	0.474	0.146
53	I^-	... 5s(2)5p(6)	1S	6918.075883	14s13p9d	0.411	0.130

Table 4. Parameters of the even-tempered wave functions. The number of STFs and the tempering parameters are shown for each cation

			1s			2p			3d		
Z	Atom		STFs	α	β	STFs	α	β	STFs	α	β
3	Li^+	(1S)	4	1.513796	1.600346						
4	Be^+	(2S)	7	0.692960	1.496893						
5	B^+	(1S)	7	0.924294	1.362999						
6	C^+	(2P)	7	0.909451	1.566711	5	0.960485	1.503732			
7	N^+	(3P)	7	1.028730	1.584961	5	1.073900	1.524892			
8	O^+	(4S)	7	1.146037	1.599637	5	1.183591	1.542339			
9	F^+	(3P)	7	1.267535	1.609940	5	1.220245	1.584573			
10	Ne^+	(2P)	7	1.386867	1.618887	5	1.282363	1.614105			
11	Na^+	(1S)	7	1.504660	1.626698	5	1.356450	1.636426			
12	Mg^+	(2S)	10	0.649998	1.429940	5	1.696697	1.587140			
13	Al^+	(1S)	10	0.732649	1.422861	5	1.142766	1.754018			
14	Si^+	(2P)	10	0.849918	1.409189	8	0.723428	1.525872			
15	P^+	(3P)	10	0.962963	1.398124	8	0.822330	1.524453			
16	S^+	(4S)	10	1.073735	1.388799	8	0.915606	1.526207			
17	Cl^+	(3P)	10	1.178537	1.381792	8	0.945126	1.552492			
18	Ar^+	(2P)	10	1.281606	1.376201	8	0.996869	1.566902			
19	K^+	(1S)	10	1.382827	1.372039	8	1.059765	1.574544			
20	Ca^+	(2S)	11	0.514641	1.499923	7	1.367846	1.421140			
21	Sc^+	(3D)	11	0.577968	1.423558	7	1.468598	1.415791	5	0.778703	1.725517
22	Ti^+	(4F)	11	0.596982	1.426733	7	1.561262	1.412842	5	0.867259	1.713032
23	V^+	(5D)	11	1.804812	1.316721	7	1.571990	1.421698	5	0.759114	1.811563
24	Cr^+	(6S)	11	1.885958	1.315859	7	1.655268	1.421027	5	0.813889	1.811540
25	Mn^+	(7S)	11	0.644787	1.436782	7	1.819945	1.410097	5	1.022206	1.734201
26	Fe^+	(6D)	11	0.655664	1.440784	7	1.904323	1.409933	5	1.030843	1.763622
27	Co^+	(3F)	11	2.106757	1.316712	7	1.897642	1.421125	5	0.868734	1.873885
28	Ni^+	(2D)	11	2.177155	1.317508	7	1.974413	1.421951	5	0.896325	1.885819
29	Cu^+	(1S)	11	2.179110	1.324270	7	2.049937	1.422997	5	0.521954	1.869469
30	Zn^+	(2S)	11	0.695558	1.454832	7	2.227206	1.412428	5	1.144130	1.821889

Table 4. (Continued)

Z	Atom	1s			2p			3d		
		STFs	α	β	STFs	α	β	STFs	α	β
31	Ga^+ (1S)	11	0.743071	1.450076	7	2.391530	1.404097	5	1.365050	1.766152
32	Ge^+ (2P)	11	0.829835	1.438533	10	0.771500	1.429568	5	1.611340	1.717628
33	As^+ (3P)	11	0.912078	1.429227	10	0.858234	1.417798	5	1.847337	1.680735
34	Se^+ (4S)	11	0.992203	1.421331	10	0.944405	1.407677	5	2.075956	1.649479
35	Br^+ (3P)	11	1.067295	1.415016	10	0.983729	1.405915	5	2.306401	1.617458
36	Kr^+ (2P)	11	1.142162	1.409351	10	1.041458	1.401619	5	2.530443	1.578894
37	Rb^+ (1S)	11	1.217300	1.404183	10	1.107265	1.396552	5	2.667444	1.496712
38	Sr^+ (2S)	13	0.525361	1.427619	10	1.242841	1.382673	5	2.102063	1.663704
39	Y^+ (1S)	13	0.573130	1.420283	10	1.052581	1.415636	5	2.278721	1.633862
40	Zr^+ (4F)	13	0.587188	1.420560	10	1.048600	1.421496	8	0.822565	1.510882
41	Nb^+ (5D)	13	1.681875	1.328907	10	1.067055	1.423002	8	0.812985	1.520000
42	Mo^+ (6S)	13	1.716191	1.328621	10	1.146422	1.416052	8	0.882535	1.507000
43	Tc^+ (7S)	13	0.644309	1.418429	10	1.286346	1.400843	8	1.026781	1.479743
44	Ru^+ (4F)	13	1.782654	1.325797	10	1.488291	1.379685	8	0.970166	1.497810
45	Rh^+ (3F)	13	1.874911	1.328980	10	1.536941	1.378034	8	1.006310	1.495843
46	Pd^+ (2D)	13	1.926696	1.333132	10	1.591834	1.377339	8	1.050981	1.491428
47	Ag^+ (1S)	13	2.060466	1.330113	10	1.621068	1.380856	8	1.096051	1.487797
48	Cd^+ (2S)	13	0.678135	1.425673	10	1.883202	1.358501	8	1.250653	1.464587
49	In^+ (1S)	13	0.710707	1.422524	10	1.862128	1.365148	8	1.389106	1.447295
50	Sn^+ (2P)	13	0.781569	1.413538	12	0.745164	1.409948	8	1.515960	1.434129
51	Sb^+ (3P)	13	0.848799	1.406002	12	0.813208	1.401441	8	1.622699	1.426932
52	Te^+ (4S)	13	0.914073	1.399438	12	0.883304	1.393516	8	1.718889	1.423107
53	I^+ (3P)	13	0.973824	1.394128	12	0.915345	1.392076	8	1.811072	1.420577
54	Xe^+ (2P)	13	1.033040	1.389289	12	0.962974	1.388525	8	1.899719	1.418953
55	Cs^+ (1S)	13	1.092549	1.384774	12	1.018021	1.384256	8	1.986113	1.417515

Table 5. Parameters of the even-tempered wave functions. The number of STFs and the tempering parameters are shown for each anion

			1s			2p			3d		
Z	Atom		STFs	α	β	STFs	α	β	STFs	α	β
1	H^-	(1S)	5	0.241331	1.463172						
3	Li^-	(1S)	8	0.107597	1.872198						
5	B^-	(3P)	8	0.429249	1.597861	6	0.191677	1.761497			
6	C^-	(4S)	8	0.562557	1.577523	6	0.194037	1.837376			
7	N^-	(3P)	8	0.688503	1.567557	6	0.362631	1.700416			
8	O^-	(2P)	8	0.814375	1.560556	6	0.427222	1.702831			
9	F^-	(1S)	8	0.940814	1.555183	6	0.504850	1.696137			
11	Na^-	(1S)	11	0.118473	1.646196	6	0.919742	1.593851			
13	Al^-	(3P)	11	0.336723	1.573173	9	0.114586	1.780254			
14	Si^-	(4S)	11	0.472017	1.521296	9	0.292723	1.693190			
15	P^-	(3P)	11	0.563939	1.500973	9	0.353883	1.669337			
16	S^-	(2P)	11	0.668387	1.481283	9	0.385305	1.523317			
17	Cl^-	(1S)	11	0.771941	1.466020	9	0.470005	1.496091			
19	K^-	(1S)	12	0.161877	1.539080	8	1.018840	1.419209			
21	Sc^-	(3F)	12	0.202058	1.522551	8	1.166843	1.428262	6	0.329312	1.842558
22	Ti^-	(4F)	12	0.197960	1.488245	8	1.274473	1.421268	6	0.435765	1.762793
23	V^-	(5D)	12	0.206454	1.488210	8	1.372472	1.417933	6	0.508550	1.731878
24	Cr^-	(6S)	12	0.214935	1.488193	8	1.468671	1.415277	6	0.582567	1.706397
25	Mn^-	(5D)	12	0.226983	1.486285	8	1.545977	1.419235	6	0.598503	1.722040
26	Fe^-	(4F)	12	0.237833	1.485144	8	1.625403	1.421769	6	0.631824	1.725994
27	Co^-	(3F)	12	0.248372	1.484242	8	1.703596	1.424217	6	0.666509	1.728888
28	Ni^-	(2D)	12	0.258650	1.483527	8	1.780565	1.426584	6	0.701600	1.731333
29	Cu^-	(1S)	12	0.268191	1.483192	8	1.858872	1.428390	6	0.742512	1.730341
31	Ga^-	(3P)	12	0.506199	1.451768	11	0.258993	1.542499	6	1.015356	1.660626
32	Ge^-	(4S)	12	0.579249	1.437947	11	0.367224	1.489776	6	1.294448	1.597504

Table 5. (Continued)

		1s			2p			3d		
Z	Atom	STFs	α	β	STFs	α	β	STFs	α	β
33	As^- (3P)	12	0.648483	1.426981	11	0.397418	1.483021	6	1.513543	1.566918
34	Se^- (2P)	12	0.718019	1.417397	11	0.446549	1.469944	6	1.717034	1.547879
35	Br^- (1S)	12	0.789938	1.408566	11	0.504253	1.456000	6	1.911096	1.536130
37	Rb^- (1S)	14	0.198879	1.493356	11	0.966190	1.373529	6	2.356165	1.499359
39	Y^- (1D)	14	0.327488	1.443762	13	0.165686	1.523019	9	0.317454	1.656707
40	Zr^- (4F)	14	0.253562	1.475055	11	0.720846	1.424804	9	0.351627	1.642092
41	Nb^- (5D)	14	0.259107	1.475355	11	0.781952	1.416654	9	0.392795	1.624242
42	Mo^- (6S)	14	0.263702	1.475999	11	0.845047	1.409002	9	0.447865	1.599011
43	Tc^- (5D)	14	0.273034	1.474692	11	0.901382	1.403394	9	0.617911	1.500448
44	Ru^- (4F)	14	0.280038	1.474338	11	0.961284	1.397721	9	0.670781	1.488042
45	Rh^- (3F)	14	0.286154	1.474319	11	1.023524	1.392223	9	0.723574	1.477285
46	Pd^- (2D)	14	0.291645	1.474525	11	1.088672	1.386809	9	0.777125	1.467668
47	Ag^- (1S)	14	0.296193	1.475062	11	1.159212	1.381159	9	0.834208	1.458482
49	In^- (3P)	14	0.503502	1.421716	13	0.292618	1.481372	9	1.014596	1.432453
50	Sn^- (4S)	14	0.572657	1.409710	13	0.420357	1.438508	9	1.081627	1.425930
51	Sb^- (3P)	14	0.638179	1.399950	13	0.455385	1.431488	9	1.158334	1.419198
52	Te^- (2P)	14	0.703674	1.391368	13	0.506341	1.421445	9	1.240814	1.412650
53	I^- (1S)	14	0.781389	1.382995	13	0.562853	1.411548	9	1.322144	1.407235

Table 6. Parameters of the doubly even-tempered wave functions. For each cation, the first line shows the number of STFs and the tempering parameters for 1s, 2p, and 3d, and the second line shows those for 2s, 3p, and 4d

			1s/2s			2p/3p			3d/4d		
Z	Atom		STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
3	Li^+	(1S)	2	1.351200	2.240376						
			2	1.008494	2.581200						
4	Be^+	(2S)	4	0.449912	2.038976						
			3	0.423500	2.828522						
5	B^+	(1S)	4	0.597591	2.103553						
			3	0.792222	2.486108						
6	C^+	(2P)	4	0.712116	2.078109	3	0.569644	1.879677			
			3	0.872379	2.567667	2	0.459084	3.528756			
7	N^+	(3P)	4	0.831384	2.039130	3	0.709428	1.834851			
			3	0.954200	2.595692	2	0.527550	3.574348			
8	O^+	(4S)	4	0.927618	2.041881	3	0.968107	1.745739			
			3	1.053940	2.594032	2	0.703332	3.340955			
9	F^+	(3P)	4	1.014221	2.060257	3	1.002476	1.756575			
			3	1.121492	2.638293	2	0.671564	3.594065			
10	Ne^+	(2P)	4	1.080471	2.089162	3	1.075184	1.763904			
			3	0.969921	2.939427	2	0.705902	3.668757			
11	Na^+	(1S)	4	1.182518	2.098416	3	1.153029	1.771659			
			3	1.069427	2.957037	2	0.754528	3.693563			
12	Mg^+	(2S)	5	0.360526	2.388695	3	1.253941	1.776656			
			5	0.463093	2.218348	2	0.875598	3.595068			
13	Al^+	(1S)	5	0.404348	2.377480	3	1.435534	1.753232			
			5	0.529990	2.202171	2	1.069467	3.414021			
14	Si^+	(2P)	5	1.152640	1.778536	4	0.681093	2.199655			
			5	0.304430	2.093223	4	0.570602	2.136166			
15	P^+	(3P)	5	1.323185	1.755648	4	0.763587	2.170749			
			5	0.350054	2.068751	4	0.650837	2.102278			
16	S^+	(4S)	5	1.460783	1.747364	4	0.825712	2.175426			
			5	0.393636	2.052582	4	0.718541	2.093754			

Table 6. (Continued)

Z	Atom		1s/2s			2p/3p			3d/4d		
			STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
17	Cl^+	(3P)	5	1.599366	1.740666	4	0.876645	2.164428			
			5	0.435152	2.041851	4	0.756229	2.100724			
18	Ar^+	(2P)	5	1.741308	1.734936	4	0.900990	2.166871			
			5	0.475473	2.034568	4	0.795875	2.101052			
19	K^+	(1S)	5	1.874004	1.733333	4	0.939418	2.166933			
			5	0.513655	2.031631	4	0.840691	2.101115			
20	Ca^+	(2S)	6	0.354878	2.079567	4	0.898926	2.201635			
			5	0.411954	2.093370	3	1.637677	2.195974			
21	Sc^+	(3D)	6	0.384237	2.040489	4	0.971165	2.183567	3	0.488251	2.684830
			5	0.439897	2.069257	3	1.731711	2.197077	2	0.887652	2.804677
22	Ti^+	(4F)	6	0.400527	2.037481	4	1.042851	2.151323	3	0.542819	2.661485
			5	0.456719	2.070642	3	1.813364	2.186552	2	0.968263	2.814060
23	V^+	(5D)	6	1.355526	1.771797	4	1.061904	2.138573	3	0.480691	2.757931
			5	2.078910	1.759314	3	1.870445	2.168356	2	0.887159	2.877562
24	Cr^+	(6S)	6	1.414333	1.771164	4	1.112722	2.106004	3	0.517554	2.732840
			5	2.129536	1.765156	3	1.821176	2.192009	2	0.944813	2.862248
25	Mn^+	(7S)	6	0.545006	2.017951	4	1.214937	2.077141	3	0.658536	2.587002
			5	0.488850	2.128585	3	1.891090	2.197804	2	1.173065	2.696085
26	Fe^+	(6D)	6	0.562774	2.018423	4	1.261371	2.079568	3	0.672845	2.588831
			5	0.501705	2.133331	3	1.944873	2.210155	2	1.201471	2.694494
27	Co^+	(3F)	6	1.572901	1.774303	4	1.226987	2.125935	3	0.551294	2.761854
			5	2.329763	1.774893	3	1.914674	2.263913	2	0.976621	2.963282
28	Ni^+	(2D)	6	1.639088	1.772771	4	1.270412	2.133690	3	0.567150	2.762557
			5	2.455066	1.769506	3	1.985396	2.275011	2	0.993757	2.986334
29	Cu^+	(1S)	6	1.647977	1.782669	4	1.313254	2.141584	3	0.586921	2.757892
			5	2.417494	1.788081	3	2.056336	2.285926	2	1.017850	3.000238
30	Zn^+	(2S)	6	0.453967	2.069975	4	1.412215	2.121736	3	0.727300	2.632207
			5	1.039440	1.986078	3	2.157948	2.282901	2	1.245331	2.837125

Table 6. (Continued)

		1s/2s			2p/3p			3d/4d		
Z	Atom	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
31	Ga^+ (1S)	6	0.500233	2.048052	4	1.461245	2.125243	3	0.878068	2.523574
		5	1.083088	1.983378	3	2.200048	2.303365	2	1.492174	2.690995
32	Ge^+ (2P)	6	0.570711	2.016759	5	0.876388	2.033504	3	1.023094	2.442051
		5	1.169582	1.968667	5	0.564036	2.178037	2	1.713092	2.595039
33	As^+ (3P)	6	0.636314	1.991025	5	0.999059	1.992112	3	1.154137	2.384106
		5	1.265187	1.950611	5	0.638639	2.140144	2	1.913831	2.526362
34	Se^+ (4S)	6	0.699923	1.971710	5	1.107045	1.965961	3	1.289659	2.329589
		5	1.330107	1.945516	5	0.708805	2.113609	2	2.131444	2.452795
35	Br^+ (3P)	6	0.756898	1.960648	5	1.165657	1.963524	3	1.363638	2.322700
		5	1.401638	1.941957	5	0.738108	2.117982	2	2.237038	2.458742
36	Kr^+ (2P)	6	0.815834	1.947127	5	1.230952	1.961141	3	1.397741	2.323107
		5	1.455052	1.940465	5	0.780555	2.115642	2	2.308737	2.455007
37	Rb^+ (1S)	6	0.874201	1.928107	5	1.558493	1.844706	3	1.646871	2.229257
		5	1.603989	1.908095	5	0.844902	2.069520	2	2.710840	2.319116
38	Sr^+ (2S)	7	0.335527	2.029866	5	1.288206	1.843533	3	1.865999	2.172995
		6	0.744752	1.964686	5	0.979078	1.878384	2	3.018033	2.259954
39	Y^+ (1S)	7	0.383785	2.005185	5	1.343109	1.842440	3	2.122986	2.097977
		6	0.764108	1.971050	5	1.006679	1.883433	2	3.417404	2.151719
40	Zr^+ (4F)	7	0.378666	2.010585	5	1.510201	1.809047	4	0.729766	2.265313
		6	0.847300	1.940613	5	1.111859	1.856158	4	0.574932	2.273549
41	Nb^+ (5D)	7	1.216558	1.803348	5	1.532989	1.815942	4	0.705339	2.297862
		6	1.896463	1.793569	5	1.149896	1.857139	4	0.547428	2.315917
42	Mo^+ (6S)	7	1.272472	1.796872	5	1.592930	1.814061	4	0.726607	2.299057
		6	1.954516	1.790734	5	1.204874	1.852797	4	0.563642	2.319024
43	Tc^+ (7S)	7	0.413433	2.014590	5	1.712240	1.798848	4	0.792771	2.273573
		6	0.944769	1.936965	5	1.276731	1.842944	4	0.616307	2.294793
44	Ru^+ (4F)	7	1.387018	1.784555	5	1.775160	1.797384	4	0.826945	2.264247
		6	2.158383	1.773400	5	1.315099	1.844511	4	0.632053	2.298010

Table 6. (Continued)

		1s/2s			2p/3p			3d/4d		
Z	Atom	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
45	Rh^+ (3F)	7	1.435260	1.781179	5	1.887390	1.785345	4	0.871266	2.253850
		6	2.197653	1.774354	5	1.376657	1.838234	4	0.660636	2.294383
46	Pd^+ (2D)	7	1.486223	1.776883	5	1.983707	1.779303	4	0.903182	2.256988
		6	2.199932	1.779455	5	1.430674	1.836812	4	0.680246	2.302762
47	Ag^+ (1S)	7	1.525508	1.775796	5	2.040066	1.779482	4	0.934366	2.258747
		6	2.247211	1.779835	5	1.480862	1.835094	4	0.699988	2.308995
48	Cd^+ (2S)	7	0.423837	2.020864	5	2.151849	1.769330	4	0.961161	2.268373
		6	1.053628	1.921463	5	1.563999	1.824348	4	0.709642	2.328436
49	In^+ (1S)	7	0.459273	2.011976	5	2.240697	1.765343	4	1.134241	2.183823
		6	1.133931	1.912217	5	1.620193	1.822596	4	0.856798	2.234812
50	Sn^+ (2P)	7	0.518401	1.984423	6	0.619575	1.944709	4	1.261180	2.139782
		6	1.252773	1.888392	6	0.557231	1.922653	4	0.948041	2.196474
51	Sb^+ (3P)	7	0.574203	1.960682	6	0.610734	1.955970	4	1.393968	2.099393
		6	1.363503	1.867818	6	0.586722	1.913012	4	1.042686	2.161273
52	Te^+ (4S)	7	0.627122	1.941888	6	0.669094	1.934475	4	1.534632	2.061791
		6	1.468754	1.851302	6	0.524240	1.957801	4	1.144493	2.127204
53	I^+ (3P)	7	0.678012	1.926315	6	0.674811	1.939019	4	1.292995	2.166479
		6	1.571012	1.837282	6	0.554956	1.946965	4	0.911217	2.265871
54	Xe^+ (2P)	7	0.727948	1.911325	6	0.727826	1.922217	4	1.353558	2.153338
		6	1.669754	1.823952	6	0.588706	1.935823	4	0.965407	2.246647
55	Cs^+ (1S)	7	0.776406	1.898860	6	0.734310	1.925210	4	1.323604	2.186253
		6	1.765855	1.812785	6	0.670836	1.900229	4	0.963106	2.266679

Table 7. Parameters of the doubly even-tempered wave functions. For each anion, the first line shows the number of STFs and the tempering parameters for 1s, 2p, and 3d, and the second line shows those for 2s, 3p, and 4d

			1s/2s			2p/3p			3d/4d		
Z	Atom		STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
1	H^-	(1S)	3	0.166357	2.194343						
			2	0.651181	1.517021						
3	Li^-	(1S)	4	0.131210	2.355937						
			4	0.095039	2.397015						
5	B^-	(3P)	4	0.284798	2.510261	3	0.192613	3.088347			
			4	0.323263	2.609492	3	0.110021	3.483492			
6	C^-	(4S)	4	0.383719	2.435234	3	0.317138	2.800943			
			4	0.442295	2.517016	3	0.196519	3.080137			
7	N^-	(3P)	4	0.465180	2.418266	3	0.280898	2.959141			
			4	0.526169	2.521502	3	0.191544	3.032261			
8	O^-	(2P)	4	0.550700	2.400125	3	0.344106	2.879835			
			4	0.619933	2.508811	3	0.235091	2.959322			
9	F^-	(1S)	4	0.638634	2.383789	3	0.425497	2.792810			
			4	0.718396	2.493300	3	0.292018	2.878698			
11	Na^-	(1S)	6	0.222637	2.052140	3	0.929530	2.467341			
			5	0.101035	2.464949	3	0.483108	2.993499			
13	Al^-	(3P)	6	0.501058	1.834509	5	0.113018	2.579098			
			5	0.285647	2.082806	4	0.222221	2.594186			
14	Si^-	(4S)	6	0.587982	1.809368	5	0.208680	2.333696			
			5	0.391414	1.988096	4	0.385609	2.327011			
15	P^-	(3P)	6	0.784640	1.740881	5	0.236251	2.323890			
			5	0.467372	1.946266	4	0.442911	2.307191			
16	S^-	(2P)	6	0.920584	1.713398	5	0.281046	2.290532			
			5	0.545993	1.913664	4	0.526027	2.265192			
17	Cl^-	(1S)	6	1.033884	1.699040	5	0.341058	2.285093			
			5	0.627087	1.887434	4	0.657660	2.212459			

Table 7. (Continued)

		1s/2s			2p/3p			3d/4d		
Z	Atom	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
19	K^- (1S)	6	0.702612	1.827417	4	0.719722	2.180019			
		6	0.113245	2.284236	4	0.771230	2.302324			
21	Sc^- (3F)	6	0.837818	1.809494	4	0.858893	2.147065	3	0.318305	3.019331
		6	0.140409	2.248478	4	0.917063	2.270393	3	0.202215	3.122719
22	Ti^- (4F)	6	0.853444	1.833717	4	0.948093	2.122495	3	0.399163	2.872322
		6	0.140796	2.276677	4	1.015930	2.241420	3	0.259770	2.965744
23	V^- (5D)	6	0.875086	1.856567	4	1.025938	2.108271	3	0.465663	2.783012
		6	0.143212	2.299442	4	1.102014	2.224408	3	0.306995	2.873146
24	Cr^- (6S)	6	0.896411	1.878537	4	1.101996	2.096961	3	0.519887	2.728310
		6	0.144891	2.323689	4	1.186814	2.210397	3	0.344357	2.820365
25	Mn^- (5D)	6	0.932620	1.888062	4	1.153172	2.099061	3	0.550263	2.712730
		6	0.150198	2.333550	4	1.239811	2.213417	3	0.362790	2.812789
26	Fe^- (4F)	6	0.966702	1.897104	4	1.221820	2.093560	3	0.589057	2.687695
		6	0.153986	2.346969	4	1.315439	2.206535	3	0.386942	2.795771
27	Co^- (3F)	6	1.001395	1.904019	4	1.278744	2.093617	3	0.629975	2.663188
		6	0.157356	2.360308	4	1.376710	2.206250	3	0.412451	2.778827
28	Ni^- (2D)	6	1.036780	1.909199	4	1.339944	2.091647	3	0.676059	2.634860
		6	0.160393	2.373481	4	1.443540	2.203347	3	0.441635	2.757123
29	Cu^- (1S)	6	1.071626	1.913626	4	1.599194	2.007207	3	0.728260	2.603874
		6	0.162718	2.387811	4	1.100085	2.144915	3	0.475656	2.730646
31	Ga^- (3P)	6	1.156099	1.912883	6	0.153280	2.264163	3	0.989829	2.442088
		6	0.183730	2.371700	5	0.518625	2.005143	3	0.654199	2.570700
32	Ge^- (4S)	6	0.774043	1.936542	6	0.258015	2.093225	3	1.105832	2.392443
		6	0.448496	2.081146	5	0.607053	1.965030	3	0.726086	2.531731
33	As^- (3P)	6	0.875419	1.907615	6	0.287829	2.068571	3	1.151747	2.388292
		6	0.508727	2.049323	5	0.654621	1.951650	3	0.749966	2.538010
34	Se^- (2P)	6	0.973632	1.882761	6	0.329428	2.035836	3	1.163803	2.395878
		6	0.566290	2.022819	5	0.692962	1.945941	3	0.771958	2.531302

Table 7. (Continued)

Z	Atom		1s/2s			2p/3p			3d/4d		
			STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
35	Br^-	(1S)	6	1.072052	1.859496	6	0.385996	1.996257	3	1.034061	2.493421
			6	0.628092	1.996157	5	0.806415	1.904778	3	0.692159	2.621069
37	Rb^-	(1S)	7	0.711967	1.778528	6	0.394810	2.009844	3	2.175560	2.061507
			7	0.110491	2.280350	5	1.000313	1.849398	3	1.570766	2.141633
39	Y^-	(1D)	7	0.528862	1.963563	7	0.075918	2.510671	5	0.232109	2.397251
			7	0.247515	2.026744	6	0.244063	2.324909	4	0.394021	2.464796
40	Zr^-	(4F)	7	0.817953	1.762730	6	0.560726	1.925351	5	0.251090	2.374347
			7	0.146338	2.214877	5	1.333264	1.781111	4	0.433011	2.428382
41	Nb^-	(5D)	7	0.851315	1.759868	6	0.588298	1.919773	5	0.265191	2.363894
			7	0.145606	2.227205	5	1.376888	1.781110	4	0.454486	2.421075
42	Mo^-	(6S)	7	0.915210	1.747934	6	0.636134	1.902790	5	0.281788	2.351559
			7	0.143729	2.240653	5	1.497381	1.760625	4	0.480032	2.411228
43	Tc^-	(5D)	7	0.957190	1.742756	6	0.684194	1.888300	5	0.297929	2.343175
			7	0.147394	2.241050	5	1.605497	1.746064	4	0.503887	2.406881
44	Ru^-	(4F)	7	0.995278	1.739133	6	0.712138	1.884870	5	0.309747	2.344013
			7	0.150541	2.242972	5	1.653587	1.746503	4	0.519765	2.414151
45	Rh^-	(3F)	7	1.027708	1.737975	6	0.717364	1.892454	5	0.323246	2.347139
			7	0.152541	2.248784	5	1.646135	1.759577	4	0.540041	2.422193
46	Pd^-	(2D)	7	1.061924	1.735673	6	0.758703	1.882675	5	0.336848	2.348080
			7	0.156447	2.248823	5	1.735443	1.750243	4	0.562659	2.424796
47	Ag^-	(1S)	7	1.091178	1.735846	6	0.791016	1.877654	5	0.363320	2.327872
			7	0.158460	2.254619	5	1.810830	1.744748	4	0.603402	2.405211
49	In^-	(3P)	7	1.138923	1.734272	7	0.177589	2.249570	5	0.554902	2.154121
			7	0.184411	2.217357	6	0.513851	2.090263	4	0.925470	2.191205
50	Sn^-	(4S)	7	1.225190	1.719087	7	0.270183	2.090698	5	0.640729	2.104425
			7	0.207616	2.182716	6	0.673447	1.973651	4	1.059608	2.135263
51	Sb^-	(3P)	7	1.343848	1.698649	7	0.297963	2.063231	5	1.026761	1.920755
			7	0.241703	2.136566	6	0.730638	1.949540	4	1.752416	1.887155

Table 7. (Continued)

			1s/2s			2p/3p			3d/4d		
Z	Atom		STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$	STFs	$\alpha/\bar{\alpha}$	$\beta/\bar{\beta}$
52	Te^-	(2P)	7	1.108201	1.740977	7	0.342340	2.018454	5	1.121358	1.895493
			7	0.205740	2.371664	6	0.816410	1.909949	4	1.911691	1.857272
53	I^-	(1S)	7	1.170997	1.730643	7	0.393365	1.975665	5	1.229106	1.870011
			7	0.228212	2.334633	6	0.911089	1.872607	4	2.104141	1.824254

find that the average errors of the ET energies are 0.0055, 0.0283, 0.262, and 0.373 millihartrees, respectively, for the first-, second-, third-, and fourth-row cations. Moreover, the ET energies are lower than the famous Clementi–Roetti results [18] with slightly smaller but fully optimized basis sets. The ET scheme is seen to be effective not only for neutrals but also for cations, despite its limited variational freedom. The DET scheme further improves the accuracy of RHF wave functions; the average errors of the DET energies for the cations are 0.0004, 0.0063, 0.061, and 0.113 millihartrees for the respective rows, and the present DET RHF wave functions are of near Hartree–Fock quality. As observed previously [11] for neutral atoms, the improvement offered by the DET method over the ET method is particularly remarkable when an atom has both very tight and diffuse orbitals of the same symmetry. For example, the DET error is smaller than the ET error by a factor of 10 for Mg^+.

The present ET and DET total energies for the anions H^-–I^-, relative to the NHF values, are summarized in Table 3. All the anion calculations were done for the experimental ground state [19] except for Sc^- and Pd^-. For these anions, the experimental ground states are reported [19] to be $\cdots$ 4s(2)3d(1)4p(1), ^{1}D and $\cdots$ 5s(1)4d(10), ^{2}S, respectively, but we could not obtain meaningful solutions in either RHF or NHF computations. The average errors in the ET energies are 0.00266, 0.0355, 0.395, and 1.064 millihartrees, respectively, for the first-, second-, third-, and fourth-row anions, and are smaller than the original Clementi–Roetti [18] errors for all the anions. For many of the third-row anions, however, the ET energies are higher than the reoptimized Clementi–Roetti [20] values, although the basis sizes are larger at least by 1s2p1d in the present ET calculations. We observe that the ET method is less effective for anions where there are both tight and diffuse orbitals in a symmetry. The DET method reduces the above errors to 0.00068, 0.0063, 0.087, and 0.112 millihartrees, and the DET is particularly successful for the fourth-row anions. The above DET errors for the anions are as small as those associated with the neutrals [11] and cations, and the present results together with the previous ones [11] provide a set of DET wave functions of near Hartree–Fock quality for all the neutral and singly-charged atoms with the $N \leqslant 54$ in their ground states (except Sc^- and Pd^-).

As discussed before [11], the success of the DET scheme comes from its increased variational flexibility relative to the ET scheme: The use of two independent sequences for exponents permits better distribution of both small and large exponents. The use of two principal quantum numbers in STFs also increases the numerical linear independence among the basis STFs. Though it uses twice as many nonlinear parameters as the ET method, the DET method is far less demanding computationally than full exponent optimizations for heavier atoms. The tempering parameters for the ET and DET wave functions for the cations and anions with $N \leqslant 54$ are listed in Tables 4–7.

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