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Improved Double-Zeta Description for the Atoms Li through Xe#

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The conventional double-zeta (DZ) approximation uses two Slater-type functions χ_{nlm}'s with different exponents for the description of each occupied atomic orbital ϕ_{nlm}, where the two principal quantum numbers n's are assumed to be the same. We show that the removal of this implicit restriction improves the DZ functions nontrivially for the ground-state atoms Li through Xe. The largest improvement 0.0267 a.u. in the atomic energy is found for Pd. The valence orbital energies are generally improved, particularly for the 4d-orbital of the fourth-row atoms. It is also found that the conventional DZ functions given in the literature can be further improved by reoptimization of the exponents.

Quantitative descriptions of the electronic structure of atoms and molecules in the Roothaan–Hartree–Fock (RHF) theory[1,2] begin with the single-zeta (SZ) or minimal-basis function, which uses a single Slater-type function (STF) χ_{nlm} to represent an occupied atomic orbital (AO) ϕ_{nlm}. The STF defined by

$$\chi_{nlm}(\vec{r};\zeta) = R_{nl}(r;\zeta)Y_{lm}(\theta,\phi), \qquad (1)$$

$$R_{nl}(r;\zeta) = [(2n)!]^{-\frac{1}{2}}(2\zeta)^{n+\frac{1}{2}}r^{n-1}\exp(-\zeta r), \qquad (2)$$

was proposed by Zener[3] and Slater[4] as an approximation to the AO ϕ_{nlm}, and the SZ approximation provides us with significant and physically-intuitive information[3—6] on atomic electronic structure and chemical bonding. However, the accuracy of the SZ approximation is rather limited, and is substantially improved by the double-zeta (DZ) approximation,[7,8] which is obtained by replacing each STF of the SZ function by two STFs that differ in their exponents ζ. Accordingly, the principal quantum number n of the two STFs $\chi_{nlm}(\vec{r};\zeta)$ and $\chi_{nlm}(\vec{r};\zeta')$ is implicitly assumed to be the same as that of the AO ϕ_{nlm}. Such DZ functions are hereafter referred to as conventional DZ functions. The optimum exponents of the conventional DZ functions have been reported by Clementi and coworkers,[9—11] and by Huzinaga and Arnau[12] for the atoms He–Xe.

In a very recent paper,[13] we demonstrated that the SZ approximation can be much improved for Al through Xe by lifting the tacit restriction that the principal quantum numbers n of the STFs χ_{nlm} match those of the AOs ϕ_{nlm}. The improvement in the atomic energy amounts to 6.4 a.u. in Xe. The valence orbital energies also improve noticeably.

In the present paper, we report that similar improvement is possible for the DZ functions by optimizing the principal quantum numbers $\{n\}$, as well as the exponents $\{\zeta\}$, of the STFs involved. In the next section, the computational method is described. Then we present reoptimized conventional DZ functions, since the literature exponents[11] could be significantly improved. The improved (unconventional) functions are reported for the atoms Li through Xe in their ground state. The conventional DZ function is confirmed to be the best for the He atom. For the Li and Be atoms, Huzinaga's modification[14] is found to be optimal, but for the rest of the atoms the present unconventional DZ functions are better with the use of the same number of basis STFs for each angular symmetry. The largest improvement of the total energy by the unconventional choice of n (relative to the reoptimized conventional one) is found to be 0.0267 a.u. for the Pd atom. Among the orbital energies of the outermost AOs of each symmetry, the largest improvement is observed for the 4d-orbitals of the fourth-row atoms. Hartree atomic units are used thoughout this paper.

Computational Method

All the present RHF calculations were performed with a modified and corrected version[15] of Pitzer's implementation[16] of the Roothaan-Bagus procedure.[17] For a given combination of STF principal quantum numbers $\{n\}$, all the exponents $\{\zeta\}$ were variationally optimized with the Powell method of conjugate directions.[18] The reoptimization of the conventional DZ exponents starting from the Clementi–Roetti values[11] was done in precisely this manner.

The variationally optimum set $\{n\}$ for the unconventional DZ function was determined by the following *ad hoc* procedures.

(i) In order to simplify the search for the optimal $\{n\}$, we decomposed the set $\{n\}$ into three subsets $\{n\}=\{n\}_s+\{n\}_p+\{n\}_d$ based on the angular momentum quantum number l. (The subsets $\{n\}_d$ and $\{n\}_p$ are null for the lighter atoms.) Following our experience in the construction of the optimal SZ functions,[13] we then determined the best set $\{n\}_l$ for each symmetry l in a decoupled manner.

(ii) For the first- and second-row atoms, the best subset $\{n\}_l$ (l=s,p) was determined by the enumeration method which examines all possible combinations of n's under the restriction of $n<5$. For a given set of $\{n\}_l$, we carried out the optimization of the exponents $\{\zeta\}$ starting from several different initial sets in order to avoid local minima in ζ-space. The results showed that the optimization of $\{n\}_p$ is

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#This paper is dedicated to the late Professor Hiroshi Kato.

Table 1. Comparison of the Conventional (Clementi–Roetti and Reoptimized) and Improved Double-Zeta Atomic Energies

Z	Atom	Clementi–Reotti	Present		Principal quantum numbers of STFs in improved DZ function
			Conventional	Improved	
3	Li(^{2}S)	−7.4327214	−7.4327223	−7.4327244	(1111)
4	Be(^{1}S)	−14.572369	−14.572371	−14.573009	(1111)
5	B (^{2}P)	−24.527920	−24.527921	−24.528710	(1112/22)
6	C (^{3}P)	−37.686749	−37.686751	−37.687586	(1112/22)
7	N (^{4}S)	−54.397951	−54.397956	−54.398789	(1112/22)
8	O (^{3}P)	−74.804323	−74.804333	−74.805164	(1112/22)
9	F (^{2}P)	−99.401309	−99.401319	−99.402117	(1122/22)
10	Ne(^{1}S)	−128.53511	−128.53512	−128.53587	(1122/22)
11	Na(^{2}S)	−161.84999	−161.85004	−161.85077	(111223/22)
12	Mg(^{1}S)	−199.60701	−199.60703	−199.60771	(111111/22)
13	Al(^{2}P)	−241.87307	−241.87325	−241.87634	(111112/2223)
14	Si(^{3}P)	−288.85116	−288.85120	−288.85381	(111112/2223)
15	P (^{4}S)	−340.71595	−340.71599	−340.71782	(111222/2223)
16	S (^{3}P)	−397.50229	−397.50232	−397.50294	(111122/2233)
17	Cl(^{2}P)	−459.47960	−459.47964	−459.48023	(111122/2233)
18	Ar(^{1}S)	−526.81511	−526.81514	−526.81572	(111112/2233)
19	K (^{2}S)	−599.16241	−599.16268	−599.16352	(11111222/2234)
20	Ca(^{1}S)	−676.75594	−676.75617	−676.75711	(11112222/2234)
21	Sc(^{2}D)	−759.72637	−759.72653	−759.72746	(11111122/2234/33)
22	Ti(^{3}F)	−848.38875	−848.38885	−848.38979	(11112222/2234/33)
23	V (^{4}F)	−942.85728	−942.85733	−942.85826	(11111122/2234/33)
24	Cr(^{7}S)	−1043.2900	−1043.2902	−1043.2910	(11111122/2224/33)
25	Mn(^{6}S)	−1149.8140	−1149.8141	−1149.8149	(11111122/2224/33)
26	Fe(^{5}D)	−1262.3715	−1262.3716	−1262.3725	(11111122/2224/33)
27	Co(^{4}F)	−1381.3205	−1381.3206	−1381.3216	(11111122/2224/33)
28	Ni(^{3}F)	−1506.7517	−1506.7519	−1506.7529	(11111122/2224/33)
29	Cu(^{2}S)	−1638.7496	−1638.7497	−1638.7507	(11111222/2224/33)
30	Zn(^{1}S)	−1777.6699	−1777.6700	−1777.6711	(11111122/2224/33)
31	Ga(^{2}P)	−1923.1110	−1923.1114	−1923.1135	(11111112/222233/33)
32	Ge(^{3}P)	−2075.2284	−2075.2289	−2075.2309	(11111112/222234/33)
33	As(^{4}S)	−2234.1207	−2234.1211	−2234.1230	(11122223/222234/33)
34	Se(^{3}P)	−2399.7563	−2399.7603	−2399.7617	(11122223/222334/33)
35	Br(^{2}P)	−2572.3415	−2572.3418	−2572.3436	(11111122/222334/33)
36	Kr(^{1}S)	−2751.9613	−2751.9615	−2751.9636	(11111122/222334/33)
37	Rb(^{2}S)	−2938.2708	−2938.2711	−2938.2732	(1111222222/222334/33)
38	Sr(^{1}S)	−3131.4652	−3131.4655	−3131.4676	(1111112222/222334/33)
39	Y (^{2}D)	−3331.6538	−3331.6552	−3331.6700	(1111112222/222334/3335)
40	Zr(^{3}F)	−3538.9633	−3538.9636	−3538.9743	(1111111223/222334/3335)
41	Nb(^{6}D)	−3753.5591	−3753.5601	−3753.5672	(1111112223/222334/3334)
42	Mo(^{7}S)	−3975.5121	−3975.5131	−3975.5219	(1111111223/223334/3334)
43	Tc(^{6}S)	−4204.7590	−4204.7594	−4204.7686	(1111111223/223334/3334)
44	Ru(^{5}F)	−4441.5000	−4441.5013	−4441.5136	(1111122233/223334/3334)
45	Rh(^{4}F)	---	−4685.8423	−4685.8563	(1111111223/223334/3334)
46	Pd(^{1}S)	---	−4937.8650	−4937.8917	(11111122/223334/3333)
47	Ag(^{2}S)	---	−5197.6559	−5197.6742	(1111111222/223334/3333)
48	Cd(^{1}S)	−5465.0971	−5465.0981	−5465.1147	(1111111222/223334/3334)
49	In(^{2}P)	−5740.1392	−5740.1403	−5740.1554	(1111222333/22222234/3334)
50	Sn(^{3}P)	−6022.9057	−6022.9063	−6022.9200	(1111222333/22222234/3334)
51	Sb(^{4}S)	−6313.4618	−6313.4623	−6313.4747	(1111222233/22222234/3334)
52	Te(^{3}P)	−6611.7622	−6611.7627	−6611.7739	(1111122223/22223344/3334)
53	I (^{2}P)	−6917.9602	−6917.9608	−6917.9711	(1111122223/22333344/3335)
54	Xe(^{1}S)	−7232.1189	−7232.1191	−7232.1294	(1111122222/22333344/3335)

critical, but $\{n\}_s=\{1\}$ is a good approximation to the best $\{n\}_s$ (see the next section for details).

(iii) For the third- and fourth-row atoms, we could no longer use the enumeration method due to the increased number of possible combinations of n's. Therefore, in the light of the results for the first- and second-row atoms, full

Table 2. Exponents of the Improved Double-Zeta Functions
See Table 1 for the Corresponding STF Principal Quantum Numbers

Z	Atom	Exponents
3	Li (^{2}S)	(4.6441, 2.4610, 0.91356, 0.56354)
4	Be(^{1}S)	(6.3753, 3.4664, 1.7783, 0.72609)
5	B (^{2}P)	(4.6051, 2.5628, 0.95878, 6.6519/2.2079, 1.0028)
6	C (^{3}P)	(5.6233, 3.3583, 1.1803, 8.0682/2.7216, 1.2539)
7	N (^{4}S)	(6.6477, 4.1593, 1.3979, 9.4765/3.2381, 1.4955)
8	O (^{3}P)	(10.405, 5.1827, 1.6219, 8.7419/3.6858, 1.6553)
9	F (^{2}P)	(8.7756, 1.8420, 12.762, 7.0079/4.1750, 1.8471)
10	Ne(^{1}S)	(9.8310, 2.0631, 14.363, 7.9215/4.6789, 2.0531)
11	Na(^{2}S)	(11.169, 6.7814, 2.4317, 1.6784, 0.62998, 12.779/5.4625, 2.5570)
12	Mg(^{1}S)	(18.806, 11.519, 7.2529, 2.7945, 1.4066, 0.64020/6.2061, 3.0412)
13	Al(^{2}P)	(16.225, 7.5817, 3.1705, 1.9074, 0.81774, 14.034/9.1514, 4.9064, 0.75888, 3.6006)
14	Si(^{3}P)	(17.355, 8.0196, 3.5389, 2.3774, 0.97255, 15.075/10.079, 5.4799, 0.95870, 4.1168)
15	P (^{4}S)	(18.588, 2.8958, 1.1169, 16.199, 10.749, 3.2504/11.127, 6.1062, 1.1458, 4.6583)
16	S (^{3}P)	(19.652, 9.0880, 3.3552, 1.2616, 17.192, 3.7195/9.5096, 5.1204, 2.3355, 1.3319)
17	Cl(^{2}P)	(20.752, 9.4987, 3.8148, 1.4013, 18.215, 4.1697/10.269, 5.6083, 2.6113, 1.4646)
18	Ar(^{1}S)	(21.846, 9.8989, 5.1174, 4.2400, 1.5381, 19.233/11.028, 6.0957, 2.8862, 1.6085)
19	K (^{2}S)	(23.068, 10.531, 4.4643, 1.7656, 0.44669, 20.354, 4.8874, 0.54672/12.091, 6.6924, 2.2245, 2.6415)
20	Ca(^{1}S)	(24.259, 11.086, 4.8254, 1.5989, 21.451, 5.2586, 1.7233, 0.66916/12.870, 7.1835, 2.5066, 2.9378)
21	Sc(^{2}D)	(25.363, 11.606, 5.0713, 2.1659, 1.1303, 0.57270, 22.481, 5.5904/ 13.628, 7.6739, 2.7126, 3.1741/4.2149, 1.7436)
22	Ti(^{3}F)	(26.597, 12.342, 5.0132, 2.6578, 23.615, 5.6911, 3.4499, 0.72117/14.380, 8.1646, 2.9103, 3.4062/4.6610, 1.9824)
23	V (^{4}F)	(27.643, 12.687, 5.8540, 2.4491, 1.2504, 0.60137, 24.600, 6.4159/15.124, 8.6542, 3.1045, 3.6359/5.0422, 2.1686)
24	Cr(^{7}S)	(28.765, 13.225, 6.3670, 2.5428, 1.1337, 0.56341, 25.648, 6.9133/15.481, 9.0174, 2.5162, 5.8942/5.1021, 2.0624)
25	Mn(^{6}S)	(29.915, 13.808, 6.6176, 2.7120, 1.3504, 0.62545, 26.717, 7.2326/16.166, 9.4875, 2.7331, 6.1854/5.7574, 2.5052)
26	Fe(^{5}D)	(31.053, 14.381, 6.9865, 2.8487, 1.4128, 0.63829, 27.778, 7.6323/16.854, 9.9659, 2.8835, 6.5536/6.0587, 2.6138)
27	Co(^{4}F)	(32.191, 14.959, 7.3541, 2.9807, 1.4680, 0.64988, 28.839, 8.0317/17.534, 10.443, 3.0306, 6.9220/6.3766, 2.7403)
28	Ni(^{3}F)	(33.310, 15.366, 9.5892, 3.1074, 1.5218, 0.66069, 29.885, 8.4485/18.205, 10.918, 3.1762, 7.2901/6.6961, 2.8690)
29	Cu(^{2}S)	(35.329, 21.188, 3.2290, 1.1374, 0.58139, 31.756, 12.106, 8.5919/18.876, 11.401, 3.2470, 7.7241/6.7869, 2.7611)
30	Zn(^{1}S)	(35.563, 16.502, 10.534, 3.3620, 1.6185, 0.68068, 31.994, 9.2427/19.524, 11.866, 3.4629, 8.0256/7.3393, 3.1341)
31	Ga(^{2}P)	(36.668, 16.991, 11.033, 8.4745, 3.5449, 1.9759, 0.84457, 33.032/25.086, 14.514, 4.7614, 0.75010, 12.141, 3.7695/7.8806, 3.5024)
32	Ge(^{3}P)	(37.776, 17.526, 11.497, 8.6764, 3.7148, 2.3135, 0.97657, 34.075/25.833, 14.943, 4.7821, 0.92315, 12.490, 4.4294/8.3995, 3.8560)
33	As(^{4}S)	(37.333, 12.855, 1.0832, 23.674, 15.601, 11.935, 5.0253, 3.7273/26.476, 15.363, 5.0458, 1.0739, 12.847, 4.7776/8.9009, 4.1983)
34	Se(^{3}P)	(40.801, 21.685, 1.2021, 36.814, 15.677, 12.253, 5.2555, 4.0164/26.527, 12.919, 4.7990, 14.643, 1.3168, 2.8073/9.3907, 4.5341)
35	Br(^{2}P)	(41.078, 19.144, 12.878, 9.2799, 4.2186, 1.3168, 37.190, 3.7386/26.814, 13.172, 5.0429, 14.830, 1.4141, 3.0054/9.8694, 4.8634)
36	Kr(^{1}S)	(38.673, 18.745, 13.805, 9.2000, 4.4820, 1.4218, 24.066, 4.0418/27.102, 13.399, 5.2916, 15.011, 1.5201, 3.2053/10.338, 5.1873)
37	Rb(^{2}S)	(46.659, 3.6799, 1.6307, 0.42797, 40.433, 30.359, 15.870, 10.702, 4.1111, 0.51944/ 25.829, 13.697, 5.5432, 21.396, 1.7628, 3.4204/10.809, 5.5131)
38	Sr(^{1}S)	(45.653, 27.292, 3.7868, 1.8447, 0.92048, 0.52886, 41.386, 16.376, 11.009, 4.2677/ 25.979, 13.892, 5.7989, 21.522, 1.9613, 3.6048/11.277, 5.8389)
39	Y (^{2}D)	(42.692, 32.459, 4.0244, 2.0030, 1.0158, 0.54919, 38.838, 16.704, 11.077, 4.5400/ 26.112, 14.002, 6.0642, 21.627, 2.0923, 3.8067/14.175, 7.6835, 1.5353, 6.2345)

Table 2. (Continued)

Z	Atom	Exponents
40	Zr(^{3}F)	(47.033, 22.123, 15.492, 12.335, 2.0855, 1.0966, 0.56506, 42.726, 6.7248, 5.5780/ 26.312, 14.086, 6.3292, 21.799, 2.2136, 4.0101/13.638, 7.3609, 1.6614, 5.5818)
41	Nb(^{6}D)	(47.968, 22.316, 16.926, 2.1995, 1.1060, 0.57912, 43.650, 14.604, 5.1343, 5.7764/ 26.581, 14.156, 6.5964, 22.034, 2.2802, 4.2182/13.356, 7.2222, 1.4485, 3.7550)
42	Mo(^{7}S)	(49.243, 23.305, 16.633, 13.442, 2.3136, 1.1330, 0.59323, 44.818, 5.4319, 6.0715/ 26.260, 6.8902, 21.824, 15.385, 2.3992, 4.4334/13.870, 7.5752, 1.7118, 2.0879)
43	Tc(^{6}S)	(50.367, 23.897, 16.959, 13.638, 2.4625, 1.2461, 0.60948, 45.876, 5.6409, 6.3026/ 26.728, 7.1717, 22.212, 15.514, 2.5711, 4.6390/14.478, 7.9766, 1.9790, 2.3791)
44	Ru(^{5}F)	(52.643, 25.637, 2.5055, 1.1428, 0.58973, 47.820, 17.868, 6.2023, 28.301, 9.6351/ 27.245, 7.4508, 22.658, 15.720, 2.6320, 4.8500/14.886, 8.2627, 1.9478, 2.3706)
45	Rh(^{4}F)	(52.595, 25.049, 17.523, 13.564, 2.6032, 1.1410, 0.58692, 49.975, 6.4817, 7.0761/ 27.771, 7.7337, 23.114, 15.938, 2.7467, 5.0589/15.393, 8.6051, 2.0675, 2.5130)
46	Pd(^{1}S)	(52.978, 25.307, 17.794, 11.341, 6.9451, 2.6376, 48.487, 6.9461/28.335, 8.0108, 23.614, 16.233, 2.7995, 5.2598, 15.576, 8.7597, 3.4152, 1.5979)
47	Ag(^{2}S)	(54.716, 26.239, 18.164, 13.406, 2.7826, 1.1336, 0.58606, 50.000, 8.7076, 7.1518/ 28.864, 8.3013, 24.077, 16.455, 2.9749, 5.4767/16.106, 9.1143, 3.6633, 1.8556)
48	Cd(^{1}S)	(55.869, 26.836, 18.563, 13.541, 2.9126, 1.4780, 0.65892, 51.081, 9.0189, 7.3635/ 29.421, 8.5911, 24.569, 16.725, 3.1462, 5.6840/16.962, 9.6512, 2.5194, 3.0270)
49	In(^{2}P)	(57.715, 27.203, 17.377, 0.77647, 52.695, 25.244, 3.7836, 11.505, 9.1037, 2.6680/ 38.334, 23.065, 16.363, 8.9083, 2.7883, 0.70784, 3.0910, 10.090/17.498, 10.004, 2.7380, 3.2601)
50	Sn(^{3}P)	(58.787, 27.680, 17.640, 0.88746, 53.712, 25.530, 3.9421, 11.805, 9.3332, 2.8853/ 39.160, 23.575, 16.694, 9.1466, 2.8586, 0.84952, 3.1564, 10.434/18.002, 10.342, 2.9438, 3.4764)
51	Sb(^{4}S)	(59.539, 27.732, 17.592, 0.99814, 54.498, 25.633, 4.0919, 2.5700, 12.180, 9.6171/ 40.334, 24.230, 17.292, 9.4563, 3.2272, 0.97202, 4.9621, 11.195/18.483, 10.668, 3.1382, 3.6775)
52	Te(^{3}P)	(60.208, 28.774, 20.627, 9.2212, 1.0892, 55.208, 11.072, 4.2606, 2.8388, 9.8651/ 44.473, 21.543, 3.6578, 1.0518, 24.421, 12.476, 10.663, 6.5928/18.948, 10.987, 3.3253, 3.8680)
53	I (^{2}P)	(61.542, 29.777, 20.677, 14.160, 1.1764, 56.424, 10.931, 4.4271, 3.0769, 10.078/ 32.392, 10.079, 27.215, 18.326, 1.8177, 1.1389, 6.8422, 4.7048/19.592, 11.399, 3.6377, 4.8829)
54	Xe(^{1}S)	(62.484, 29.987, 21.451, 9.3886, 1.2602, 57.350, 11.503, 9.3860, 4.6274, 3.3128/ 32.984, 10.379, 27.746, 18.667, 1.9620, 1.2278, 7.0451, 4.9010/20.062, 11.719, 3.8252, 5.0857)

optimization of $\{n\}_p$ and $\{n\}_d$ was performed for the atoms K–Zn, and only for $\{n\}_d$ in Ga–Xe. For smaller l's, we started from a trial set $\{n\}_l=\{l+1\}$ and modified (raised) some n's so as to increase the computational linear independence among the relevant STFs until no further improvement in the atomic energy was obtained. Even-tempered augmented DZ functions[19] were used for an initial guess of the exponents.

Results and Discussion

Reoptimized Conventional DZ Functions. Since we needed the conventional DZ results as our starting point in constructing improved DZ functions, we reoptimized the exponents of the DZ functions reported in Ref. 11. Unfortunately, we found that the literature exponents are not fully optimum. The atomic energies from the present ζ-reoptimization are compared in Table 1 with previous results[11] for the atoms Li–Xe in their ground state. An improvement in the atomic energy is found for all these atoms, the largest being 0.0040 a.u. for the Se atom. New exponents for the conventional DZ functions are given in the Appendix.

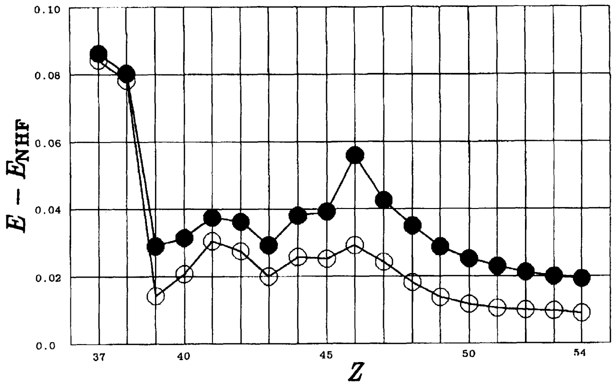

Fig. 1. Atomic energy errors $E-E_{\rm NHF}$ of the conventional (●) and improved (○) DZ functions with respect to the numerical HF value for the fourth-row atoms.

Another point to be noted is that the Clementi–Roetti DZ function[11] for the Rh atom in the [Kr]5s^{1}4d^8 (^{4}F) state is incorrect. The same was true for their

Table 3. Exponents of the Reoptimized Conventional Double-Zeta Functions

Z	Atom	Exponents
3	Li (^{2}S)	(4.7026, 2.4867, 1.9810, 0.67152)
4	Be(^{1}S)	(5.5473, 3.3485, 1.0085, 0.58594)
5	B (^{2}P)	(6.5052, 4.2354, 1.4176, 0.88703/2.2106, 1.0041)
6	C (^{3}P)	(7.4343, 5.0963, 1.8432, 1.1728/2.7226, 1.2545)
7	N (^{4}S)	(8.3763, 5.9397, 2.2804, 1.4451/3.2383, 1.4958)
8	O (^{3}P)	(9.3066, 6.7585, 2.7247, 1.7097/3.6856, 1.6554)
9	F (^{2}P)	(10.274, 7.5754, 3.1699, 1.9697/4.1747, 1.8470)
10	Ne(^{1}S)	(11.267, 8.3938, 3.6155, 2.2264/4.6784, 2.0530)
11	Na(^{2}S)	(12.235, 9.1660, 4.0285, 2.6125, 1.1706, 0.72417/5.4623, 2.5570)
12	Mg(^{1}S)	(13.175, 9.8988, 4.4607, 3.0323, 1.4631, 0.88734/6.2061, 3.0413)
13	Al(^{2}P)	(14.135, 10.630, 4.8761, 3.4400, 1.7755, 1.1028/7.3874, 3.7474, 2.0611, 0.98119)
14	Si(^{3}P)	(15.081, 11.308, 5.3398, 3.9055, 2.0723, 1.2949/7.9976, 4.1496, 1.8475, 1.0788)
15	P (^{4}S)	(16.027, 11.942, 5.8655, 4.4448, 2.3637, 1.4807/8.7536, 4.6343, 2.0680, 1.2293)
16	S (^{3}P)	(16.983, 12.542, 6.4854, 5.0433, 2.6332, 1.6536/9.5095, 5.1205, 2.3357, 1.3321)
17	Cl(^{2}P)	(17.958, 13.141, 7.1770, 5.6313, 2.8982, 1.8223/10.269, 5.6083, 2.6114, 1.4648)
18	Ar(^{1}S)	(18.949, 13.760, 7.8811, 6.1788, 3.1645, 1.9905/11.028, 6.0957, 2.8863, 1.6087)
19	K (^{2}S)	(19.979, 14.499, 8.3266, 6.6766, 3.5067, 2.3436, 1.1964, 0.72415/11.820, 6.5959, 3.2073, 1.9246)
20	Ca(^{1}S)	(20.992, 15.202, 8.8078, 7.1737, 3.8039, 2.6581, 1.4314, 0.86461/12.590, 7.0886, 3.4863, 2.1940)
21	Sc(^{2}D)	(21.989, 15.849, 9.4225, 7.6719, 4.0581, 2.8293, 1.5361, 0.91169/13.321, 7.5732, 3.7636, 2.3663/4.2146, 1.7436)
22	Ti(^{3}F)	(22.985, 16.482, 10.061, 8.1598, 4.3175, 2.9904, 1.6219, 0.94865/14.036, 8.0550, 4.0456, 2.5333/4.6609, 1.9825)
23	V (^{4}F)	(23.982, 17.104, 10.712, 8.6389, 4.5789, 3.1506, 1.7018, 0.98256/14.738, 8.5344, 4.3278, 2.6981/5.0422, 2.1687)
24	Cr(^{7}S)	(24.970, 17.680, 11.425, 9.1051, 4.8319, 3.2282, 1.7375, 0.95722/15.398, 9.0052, 4.5917, 2.7700/5.1016, 2.0621)
25	Mn(^{6}S)	(25.973, 18.315, 12.038, 9.5760, 5.1040, 3.4702, 1.8484, 1.0435/16.107, 9.4866, 4.8909, 3.0219/5.7573, 2.5051)
26	Fe(^{5}D)	(26.969, 18.908, 12.701, 10.038, 5.3621, 3.6305, 1.9272, 1.0764/16.777, 9.9602, 5.1686, 3.1837/6.0585, 2.6137)
27	Co(^{4}F)	(27.965, 19.486, 13.371, 10.495, 5.6211, 3.7898, 2.0009, 1.1065/17.436, 10.432, 5.4468, 3.3439/6.3764, 2.7401)
28	Ni(^{3}F)	(28.961, 20.054, 14.045, 10.949, 5.8798, 3.9484, 2.0724, 1.1355/18.086, 10.902, 5.7248, 3.5031/6.6958, 2.8689)
29	Cu(^{2}S)	(29.946, 20.551, 14.729, 11.386, 6.1447, 4.0393, 1.9938, 1.0323/18.692, 11.364, 5.9775, 3.5671/6.7866, 3.7609)
30	Zn(^{1}S)	(30.952, 21.147, 15.405, 11.850, 6.3966, 4.2640, 2.2085, 1.1895/19.360, 11.839, 6.2804, 3.8187/7.3390, 3.1340)
31	Ga(^{2}P)	(31.959, 21.851, 15.737, 12.294, 6.7431, 4.5831, 2.4527, 1.3938/20.136, 12.345, 6.6308, 4.1545, 1.9934, 1.0365/7.8807, 3.5025)
32	Ge(^{3}P)	(32.966, 22.536, 16.120, 12.740, 7.0887, 4.9051, 2.6798, 1.5651/20.833, 12.829, 6.9285, 4.4292, 2.2438, 1.2259/8.3995, 3.8560)
33	As(^{4}S)	(33.973, 23.211, 16.527, 13.189, 7.4366, 5.2314, 2.9012, 1.7242/21.523, 13.311, 7.2162, 4.6998, 2.4735, 1.3927/8.9008, 4.1983)
34	Se(^{3}P)	(34.980, 23.875, 16.953, 13.638, 7.7834, 5.5577, 3.1135, 1.8737/22.202, 13.791, 7.4918, 4.9630, 2.6877, 1.4930/9.3909, 4.5342)
35	Br(^{2}P)	(35.988, 24.537, 17.379, 14.087, 8.1386, 5.8897, 3.3255, 2.0189/22.876, 14.270, 7.7579, 5.2201, 2.9035, 1.6124/9.8695, 4.8634)
36	Kr(^{1}S)	(36.995, 25.198, 17.794, 14.536, 8.5082, 6.2282, 3.5367, 2.1614/23.544, 14.748, 8.0148, 5.4693, 3.1177, 1.7393/10.339, 5.1873)
37	Rb(^{2}S)	(38.022, 26.008, 17.990, 15.032, 9.1175, 6.6864, 3.8607, 2.5023, 1.3680, 0.79906/24.232, 15.231, 8.2764, 5.7222, 3.4005, 2.0172/10.809, 5.5132)
38	Sr(^{1}S)	(39.038, 26.721, 18.333, 15.518, 9.6402, 7.0717, 4.0788, 2.7449, 1.5867, 0.93789/24.900, 15.711, 8.5224, 5.9555, 3.6407, 2.2483/11.277, 5.8390)
39	Y (^{2}D)	(40.020, 27.419, 18.716, 16.012, 10.169, 7.4415, 4.2604, 2.8897, 1.6941, 0.9905/ 25.568, 16.190, 8.7639, 6.1942, 3.8653, 2.4072/12.981, 6.9832, 4.4315, 1.8704)

Table 3. (Continued)

Z	Atom	Exponents
40	Zr(^{3}F)	(41.064, 28.101, 19.076, 16.496, 10.751, 7.7978, 4.4457, 3.0237, 1.7874, 1.0375/26.203, 16.662, 9.0067, 6.4197, 4.0818, 2.5520/12.986, 6.9661, 3.7669, 1.8555)
41	Nb(^{6}D)	(42.076, 28.778, 19.494, 16.998, 11.333, 8.1432, 4.6565, 3.1343, 1.8491, 1.0653/26.819, 17.130, 9.2456, 6.6384, 4.2788, 2.6302/13.276, 7.1755, 3.5857, 1.7142)
42	Mo(^{7}S)	(43.088, 29.443, 19.921, 17.501, 11.900, 8.4796, 4.8486, 3.2558, 1.9292, 1.0992/27.433, 17.599, 9.4768, 6.8339, 4.4999, 2.7649/13.765, 7.5116, 3.8015, 1.8566)
43	Tc(^{6}S)	(44.102, 30.149, 20.100, 18.052, 12.746, 8.8279, 5.0075, 3.3793, 2.0049, 1.1396/28.052, 18.068, 9.7022, 6.9993, 4.7509, 2.9717/14.339, 7.8943, 4.1659, 2.1835)
44	Ru(^{5}F)	(45.113, 30.795, 20.639, 18.568, 13.236, 9.1452, 5.2288, 3.4954, 2.0274, 1.1239/28.632, 18.529, 9.9322, 7.1650, 4.9446, 3.0389/14.716, 8.1704, 4.2266, 2.0734)
45	Rh(^{4}F)	(46.126, 31.460, 21.018, 19.127, 13.896, 9.4683, 5.4206, 3.6135, 2.0690, 1.1334/29.212, 18.990, 10.160, 7.2953, 5.1696, 3.1739/15.189, 8.4996, 4.4464, 2.1896)
46	Pd(^{1}S)	(47.116, 32.056, 21.125, 19.495, 14.672, 9.7541, 5.5972, 3.6436/29.762, 19.444, 10.390, 7.4067, 5.3501, 3.2269/15.574, 8.7886, 4.5481, 2.1302)
47	Ag(^{2}S)	(48.150, 32.773, 21.819, 20.291, 15.164, 10.102, 5.8083, 3.8527, 2.1441, 1.1505/30.339, 19.905, 10.623, 7.4709, 5.6266, 3.4416/16.125, 9.1535, 4.8850, 2.4244)
48	Cd(^{1}S)	(49.170, 33.462, 21.620, 21.421, 16.126, 10.427, 5.9595, 3.9635, 2.3190, 1.2802/30.900, 20.362, 10.857, 7.4704, 5.8993, 3.6513/16.658, 9.5096, 5.1946, 2.6920)
49	In(^{2}P)	(50.183, 34.089, 22.946, 21.501, 16.215, 10.743, 6.1887, 4.1861, 2.5297, 1.4567/31.571, 20.847, 11.065, 6.5072, 6.5071, 4.0773, 2.1219, 1.1381/17.191, 9.8652, 5.5014, 2.9634)
50	Sn(^{3}P)	(51.212, 34.924, 22.939, 22.691, 16.770, 11.065, 6.5970, 4.3895, 2.7220, 1.6063/32.144, 21.312, 11.339, 6.8196, 6.8204, 4.3296, 2.3408, 1.3103/17.710, 10.214, 5.7891, 3.2163)
51	Sb(^{4}S)	(52.193, 35.223, 24.821, 22.131, 16.341, 11.375, 6.6392, 4.6316, 2.9110, 1.7463/32.708, 21.775, 11.609, 7.1401, 7.1404, 4.5840, 2.5426, 1.4633/18.220, 10.558, 6.0625, 3.4556)
52	Te(^{3}P)	(53.198, 35.802, 25.546, 22.540, 16.521, 11.693, 6.8535, 4.8448, 3.0886, 1.8753/33.253, 22.232, 11.873, 7.4390, 7.4389, 4.8254, 2.7225, 1.5524/18.723, 10.900, 6.3284, 3.6888)
53	I (^{3}P)	(54.201, 36.367, 26.228, 22.942, 16.694, 12.012, 7.0671, 5.0594, 3.2647, 2.0003/33.796, 22.689, 12.134, 7.7527, 7.7527, 5.0744, 2.9050, 1.6597/19.220, 11.238, 6.5841, 3.9125)
54	Xe(^{1}S)	(55.205, 36.955, 26.854, 23.375, 16.929, 12.332, 7.2730, 5.2661, 3.4390, 2.1227/34.338, 23.145, 12.389, 8.0849, 8.0847, 5.3307, 3.0848, 1.7741/19.709, 11.572, 6.8315, 4.1284)

near-HF result with a 11s7p5d STF basis set (see also Refs. 20 and 21). The incorrect Clementi–Roetti results for both the DZ and near-HF wave functions can be obtained by an incorrect reversal of sign for one of the vector coupling constants.

Improved DZ Functions. Optimization of the STF parameters $\{n\}$ and $\{\zeta\}$ in the DZ approximation was performed for the atoms He through Xe in their experimental ground states. For the He atom, we confirmed that the conventional DZ function is the best. However, unconventional DZ functions are found to be better than the conventional ones for all the other atoms. Table 1 compares the atomic energies E from the conventional (both literature[11)] and reoptimized) and unconventional DZ functions for the atoms Li–Xe. The composition of our improved DZ functions is also shown there, where the notation(···/··/·) stands for the principal quantum numbers of the constituent STFs and the symbol / separates different l's in the order: s, p, and d. Table 1 shows that the improvement in the atomic energy is not monotonic with respect to the atomic number Z, and is largest (0.0267 a.u.) for Pd. The typical improvement is depicted in Fig. 1 for the fourth-row atoms, where the reoptimized conventional and improved DZ energies E relative to the numerical HF values[20,22—24)] E_{NHF} are plotted.

Table 2 shows the exponents $\{\zeta\}$ of our unconventional DZ functions. They are presented in the order that corresponds to the STFs specified in the last column of Table 1. The virial ratio did not deviate from its exact value (-2) by more than 1×10^{-7} in any of the present calculations; this suggests good local convergence of our optimization.

For the first- and second-row atoms, Huzinaga[14)] proposed unconventional DZ functions with $\{n\}_s=\{1\}$ and $\{n\}_p=\{2\}$. The present optimization verifies that his choice is the best for Li and Be. The choice $\{n\}_p=\{2\}$ is best for the atoms B–Mg, but not for the atoms Al–Ar. This is the origin of the increased atomic energy in Huzinaga's DZ functions for the atoms S–Ar.[14)] For the s-space of the atoms B–Ar, the best $\{n\}_s$ includes a few 2s STFs in addition to the dominant 1s contribution, but our examination has shown that $\{n\}_s=\{1\}$ is a good and simple approximation to the best $\{n\}_s$. (The associated energy increase is 0.00002 a.u. at most.) These results of the full and simplified optimization of $\{n\}$ for the atoms Li–Ar suggest that the greatest improvement in the unconventional DZ functions comes from optimization of $\{n\}_l$ for the largest l, partly because this subspace contains the fewest STFs. Note that for F and Ne, the optimal $\{n\}$ is exactly the same as the conventional $\{n\}$. This implies that the conventional DZ functions for these atoms correspond to higher local minima in the ζ-space.

The choice of $\{n\}_d=\{3\}$ is good for the third- and fourth-row atoms except for the heavier atoms Y–Rh and Cd–Xe where a 4d or 5d STF contributes. The best p-space is described by the 2p, 3p, and 4p STFs, but there is no definite trend in their relative weights. For the s-space, the empirical choice of $\{n\}_s=\{1\}$ has been again found to improve the atomic energy. However, replacement of some 1s STFs with 2s or 3s STFs increases the numerical linear independence of the s-type STFs and lowers the atomic energy slightly.

As suggested above, a larger improvement in the atomic energy was obtained from the optimization of $\{n\}_l$ with a larger l. Therefore, the largest improvement in the unconventional DZ functions is seen for the fourth-row atoms. We see a general tendency that the use of n's lower than the conventional n's is better, but we cannot find any systematics in the best $\{n\}$ summarized in Table 1.

We have also examined the accuracy of the orbital energies ϵ of the valence orbitals. The unconventional DZ functions give better agreement with the numerical HF values[22—24] ϵ_{NHF}. The largest improvement is found for the fourth-row atoms: The average absolute error is reduced from 0.00537 to 0.00281 a.u., form 0.00871 to 0.00567 a.u., and 0.00985 to 0.00615 a.u., respectively, for the outermost s, p, and d AOs. However, the opposite has been also found for several atoms. For example, the outermost p orbital energy is slightly worsened for the atoms B–Mg. All the valence orbital energies are worsened for the atoms Si, P, K, Ca, Ge, As, and Zr. These results suggest limits to the improvements possible within the DZ approximation.

Concluding Remarks

We have reported the improvement of the DZ approximation by the variational choice of the STF principal quantum numbers $\{n\}$ for the atoms Li–Xe. The largest improvement in the atomic energy has been found for the fourth-row atoms and the energy gap between the DZ and numerical HF results has been considerably reduced (see Fig. 1). The valence orbital energies have been generally improved, especially for the fourth-row atoms, but not for all the atoms examined. We hope the improved DZ functions presented in this study will be useful for molecular calculations where the use of a larger basis set is not feasible.

Appendix

The conventional DZ functions reported in the literature[11] can be improved by further optimization of the STF exponents ζ. The improved atomic energies are listed in Table 1 and compared with the literature values. The corresponding exponents are summarized in Table 3 for the atoms Li–Xe in their ground state.

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