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Optimal single-zeta description for the atoms Al through Xe

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Summary. The conventional single-zeta (SZ) approximation in Roothaan–Hartree–Fock calculations of atoms is based upon a single Slater-type function (STF) χ_{nlm} for the description of each occupied atomic orbital ϕ_{nlm} with quantum numbers n, l, m. We demonstate that the SZ approximation can be improved for Al through Xe by lifting the tacit restriction that the principal quantum numbers of the STF match those of the atomic orbitals. The resulting improvements in the atomic energies range from 0.0015 a.u. in Al to 6.4 a.u. in Xe. The valence orbital energies also improve noticeably. Some of the unphysical positive d-orbital energies in the conventional SZ description of transition metal atoms turn negative in our improved SZ approximation.

Key words: Single-zeta wave functions – Minimal basis sets – Slater type functions – Ground-state neutral atoms

1. Introduction

In the Roothaan–Hartree–Fock (RHF) description [1] of atoms, the single-zeta (SZ) or minimal basis approximation is the simplest approximation which describes the electronic structure semiquantitatively. The SZ approximation uses a single Slater-type function (STF) χ_{nlm} for each occupied atomic orbital ϕ_{nlm} with quantum numbers n, l, m. The STF is defined by:

$$\chi_{nlm}(\underset{\sim}{r};\zeta) = R_{nl}(r;\zeta)Y_{lm}(\theta,\phi),$$
$$R_{nl}(r;\zeta) = [(2n)!]^{-1/2}(2\zeta)^{n+(1/2)}r^{n-1}\exp(-\zeta r). \tag{1}$$

The SZ approximation originated in the landmark papers by Zener and Slater [2, 3].

Minimal STF basis sets are of interest even though they do not give quantitatively accurate results. They provide us with significant physical intuition such as effective nuclear charges and screening constants [2, 3]. After fitting to Gaussians, as in the STO-3G basis sets [4], they may be useful for very large molecules [4] for which more elaborate calculations are not feasible even with current computer technology. Improved *ab initio* minimal basis sets of STF also may be useful for improvements in the calibration of semiempirical theories that use minimal basis sets, such as the various neglect of differential overlap methods [5, 6]. Finally, improved minimal basis sets could serve as the starting point for the construction of more flexible STF basis sets which might prove useful in density functional calculations as carried out by the Amsterdam and Calgary groups [7, 8].

Because of the small number of basis functions in the SZ approximation, the optimality of the constituent STFs is particularly important. An extensive examination of the optimum STF exponents $\{\zeta\}$ was carried out by Clementi and coworkers for the atoms He through Xe [9–12]. Some modifications of these atomic exponents have been proposed for molecular calculations (see, e.g., [4]).

However, little attention has been paid to the choice of the principal quantum numbers of the STF. It is common practice to approximate an atomic orbital (AO) ϕ_{nlm} by an STF χ_{nlm} with the same quantum numbers. We shall refer to the SZ wave function resulting from this prescription as the conventional SZ wave function. The tacit assumption that the principal quantum numbers of the AO and the corresponding STF be the same is unnecessarily restrictive because the radial part of an STF is just a simple nodeless approximation to a hydrogenic function. Cook [13] made a comparative analysis of STFs and hydrogenic functions, and proposed, for the atoms Na–Kr, the use of 2*s* and 2*p* STFs for *s*- and *p*-subshells with $n \geqslant 2$. His modification led to a nontrivial improvement in the valence orbital energies, but the total energies were not always improved and sometimes worsened. The latter feature is quite undesirable because RHF theory, and its SZ approximation, rests upon the variational principle.

In the present paper, we study the variational optimization of *both* the principal quantum numbers $\{n\}$ and the exponents $\{\zeta\}$ of STFs $\{\chi_{nlm}(\underline{r}; \zeta)\}$ involved in the SZ description of the atoms He–Xe. The $\{n\}$ are limited to integer values in this work. For the atoms He–Mg, the conventional SZ function is found to be the best, but an unconventional SZ function with an improved energy is found for each of the atoms Al through Xe; the improvement amounts to 6.4 a.u. for the Xe atom. Moreover, a remarkable improvement in the valence orbital energies is obtained for almost all cases. For some transition metal atoms, the present SZ function gives a negative orbital energy for the outermost *d*-orbital in contrast to the unphysical positive orbital energy predicted by the corresponding conventional SZ function. Hartree atomic units are used throughout this paper.

2. Method

All the present RHF calculations were performed with a modified and corrected version [14] of Pitzer's implementation [15] of the Roothaan–Bagus procedure [16]. For a given combination of STF principal quantum numbers $\{n\}$, all the exponents $\{\zeta\}$ were variationally optimized with the Powell method of conjugate directions [17], and the variationally optimum set $\{n\}$ was determined by the following trial-and-error procedure.

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 azimuthal quantum number *l*. (The subsets $\{n\}_d$ and $\{n\}_p$ are null for the lighter atoms.) Then starting from $\{n\}$ for the conventional SZ function, we determined the best $\{n\}$ for each symmetry in a "decoupled" manner. A few "coupled" searches of $\{n\}_l$ and $\{n\}_{l'}$ were made to verify that the above decoupled procedure did not change the best combination of $\{n\}$. Moreover, we imposed the restriction $n < 5$ on the basis of preliminary tests.

Despite these simplifications for the best $\{n\}$ search, we had to recognize that there are several local minima in the $\{\zeta\}$ space for a given combination of $\{n\}$. Therefore, we tried various sets of initial values of $\{\zeta\}$. In the case of the fourth-row atoms, we performed about 400 optimizations with different sets $\{n\}$ and different initial sets $\{\zeta\}$ for each atom. We think the majority of the improved SZ functions reported below are at the global minimum.

3. Results and discussion

The variational optimization of the STF parameters $\{n\}$ and $\{\zeta\}$ in the SZ approximation has been performed for the atoms He through Xe in their experimental ground states. For the atoms He–Mg, we have confirmed that the conventional SZ function is the best. However, superior unconventional SZ functions have been found for the other atoms. Table 1 presents a comparison of the energies of our unconventional SZ functions for Al–Xe with conventional ones. (The conventional SZ functions have been also reoptimized in the present study and some of them have slightly lower energies than the literature values [9–12].) Table 1 shows that the improvement in the total energy increases with atomic number Z from 0.0015 a.u. for Al to 6.4 a.u. for Xe.

Table 2 shows the detailed composition and parameters of our unconventional SZ functions. The notation (.../../.) stands for the principal quantum numbers for the constituent s-, p-, and d-type STFs. The corresponding exponents are given in a similar manner. In all these calculations, the virial ratio did not deviate from its exact value (-2) by more than 1×10^{-7} lending support to our claim that our exponents have been optimized sufficiently. It is rather difficult to derive a systematic rule for the best combination of $\{n\}$ from Table 2. However, the following rough trends can be discerned:

(i) For ns $(n \geqslant 2)$ AOs, $3s$ STFs give a good description generally. This statement holds for Ca–Xe. For the lighter atoms Al–K, $1s$ and $2s$ STFs play a definite role, while for the heavier atoms In–Xe, a $4s$ STF contributes slightly. The recommendation [18, 19] for the use of STF with the smallest n (i.e., $1s$ STF for s AOs, $2p$ STF for p AOs, etc.) is seen to be non-optimal.

(ii) For p AOs, $2p$ STFs are suitable. This result agrees with Cook's modification [13]. For heavier atoms (As-Xe), however, $3p$ STFs become more appropriate for the description of np $(n \geqslant 3)$ AOs.

(iii) For d AOs, $3d$ STFs are the best with the sole exception of Y.

It is interesting that except for the atoms S–K, only a single $1s$ STF is involved and its exponent is approximately $Z - 0.3$ in accord with the Slater rule [2, 3]. When there is one $1s$ STF and all the other s-STFs have $n \geqslant 2$ as in many of our unconventional SZ functions, then the electron-nuclear cusp condition is satisfied if the exponent of the $1s$ STF is the atomic number Z. A more remarkable point is that an ns STF is not always used to represent the ns AO. In the atoms Nb, Mo, Rh, and Cd, for example, the $2s$ STF appears as the dominant component of the $5s$ AO, and a $3s$ STF is used to describe the $2s$ AO.

Table 1. Comparison of the conventional and improved single-zeta atomic energies

Atom		Atomic energy		Energy
		Conventional	Present	improvement
Al	(^2P)	−241.15376	−241.15525	0.00149
Si	(^3P)	−288.08996	−288.09291	0.00295
P	(^4S)	−339.90988	−339.91410	0.00422
S	(^3P)	−396.62762	−396.65329	0.02567
Cl	(^2P)	−458.52369	−458.58386	0.06017
Ar	(^1S)	−525.76525	−525.86636	0.10111
K	(^2S)	−598.08987	−598.16047	0.07060
Ca	(^1S)	−675.63390	−675.72571	0.09181
Sc	(^2D)	−758.40414	−758.55760	0.15346
Ti	(^3F)	−846.81561	−847.03742	0.22181
V	(^4F)	−940.97197	−941.27626	0.30429
Cr	(^7S)	−1040.6768	−1041.1118	0.4350
Mn	(^6S)	−1147.1067	−1147.5968	0.4901
Fe	(^5D)	−1259.0855	−1259.6777	0.5922
Co	(^4F)	−1377.3744	−1378.0759	0.7015
Ni	(^3F)	−1502.0487	−1502.8662	0.8175
Cu	(^2S)	−1632.3355	−1633.3292	0.9937
Zn	(^1S)	−1771.1509	−1772.2205	1.0696
Ga	(^2P)	−1916.5167	−1917.6290	1.1123
Ge	(^3P)	−2068.5139	−2069.6880	1.1741
As	(^4S)	−2227.2649	−2228.5308	1.2659
Se	(^3P)	−2392.7274	−2394.1472	1.4198
Br	(^2P)	−2565.1131	−2566.6969	1.5838
Kr	(^1S)	−2744.5197	−2746.2772	1.7575
Rb	(^2S)	−2930.6932	−2932.5795	1.8863
Sr	(^1S)	−3123.7176	−3125.7516	2.0340
Y	(^2D)	−3324.7806	−3326.9999	2.2193
Zr	(^3F)	−3531.3183	−3533.7825	2.4642
Nb	(^6D)	−3745.2568	−3748.0494	2.7926
Mo	(^7S)	−3966.8957	−3969.9453	3.0496
Tc	(^6S)	−4196.0537	−4199.2775	3.2238
Ru	(^5F)	−4432.1153	−4435.7609	3.6456
Rh	(^4F)	−4676.0291	−4680.0025	3.9734
Pd	(^1S)	−4927.7307	−4932.6095	4.8788
Ag	(^2S)	−5186.8953	−5191.5861	4.6908
Cd	(^1S)	−5454.1908	−5459.0990	4.9082
In	(^2P)	−5729.0987	−5734.2013	5.1026
Sn	(^3P)	−6011.6720	−6017.0059	5.3339
Sb	(^4S)	−6302.0043	−6307.5800	5.5757
Te	(^3P)	−6600.0387	−6605.8807	5.8420
I	(^2P)	−6905.9462	−6912.0649	6.1187
Xe	(^1S)	−7219.7923	−7226.1971	6.4048

Figures 1a and b respectively show the ratios of the energies of the highest *s*- and *p*-AOs computed in the SZ approximation to the corresponding numerical Hartree–Fock limit values [20, 21]. Figure 1a shows clearly that the unconventional SZ functions lead to noticeably improved valence *s*-orbital energies,

Table 2. Parameters of the improved single-zeta functions

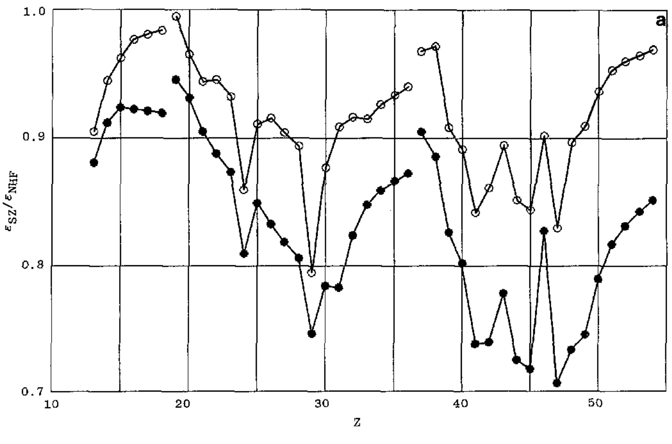
Atom		Principal quantum numbers	Exponents
Al	(^2P)	(123/22)	(12.59110, 4.10601, 1.37692/4.48407, 0.91237)
Si	(^3P)	(123/22)	(13.57463, 4.50879, 1.64169/4.97188, 0.97139)
P	(^4S)	(123/22)	(14.55790, 4.91054, 1.88953/5.47327, 1.11756)
S	(^3P)	(112/22)	(15.55678, 1.07329, 5.23989/5.97268, 1.25970)
Cl	(^2P)	(112/22)	(16.54333, 1.22055, 5.63380/6.47162, 1.41171)
Ar	(^1S)	(112/22)	(17.52995, 1.36548, 6.02763/6.96854, 1.56754)
K	(^2S)	(1123/22)	(18.51934, 1.56381, 6.41025, 0.70614/7.46772, 1.80666)
Ca	(^1S)	(1333/23)	(19.70586, 10.26552, 3.16067, 0.85503/8.01047, 2.87308)
Sc	(^2D)	(1333/23/3)	(20.70690, 10.87025, 3.40469, 0.90092/8.51715, 3.12332/2,33454)
Ti	(^3F)	(1333/22/3)	(21.70828, 11.47176, 3.63918, 0.95458/8.95710, 2.38335/2.74745)
V	(^4F)	(1333/22/3)	(22.70963, 12.07485, 3.86127, 0.98411/9.45690, 2.54765/3.01924)
Cr	(^7S)	(1233/22/3)	(23.71084, 0.61038, 12.67887, 4.04703/9.96212, 2.67413/3.04662)
Mn	(^6S)	(1333/22/3)	(24.71269, 13.27991, 4.29294, 1.03707/10.45477, 2.86579/3.52608)
Fe	(^5D)	(1233/22/3)	(25.71429, 0.74096, 13.88399, 4.49908/10.95324, 3.02589/3.73969)
Co	(^4F)	(1233/22/3)	(26.71602, 0.75558, 14.48639, 4.71220/11.45122, 3.18332/3.96382)
Ni	(^3F)	(1233/22/3)	(27.71783, 0.76958, 15.08857, 4.92332/11.94885, 3.33912/4.18756)
Cu	(^2S)	(1233/22/3)	(28.71939, 0.63684, 15.69222, 5.10905/12.45388, 3.46071/4.22131)
Zn	(^1S)	(1233/22/3)	(29.72164, 0.79601, 16.29229, 5.33991/12.94319, 3.64605/4.63546)
Ga	(^2P)	(1333/222/3)	(30.72389, 16.89180, 5.59764, 1.39582/13.43437, 3.84195, 0.69962/5.03237)
Ge	(^3P)	(1333/223/3)	(31.72606, 17.49234, 5.84919, 1.58758/13.92235, 4.04423, 1.24006/5.41429)
As	(^4S)	(1333/233/3)	(32.72801, 18.09572, 6.10124, 1.74822/14.52912, 5.93858, 1.43441/5.76463)
Se	(^3P)	(1333/233/3)	(33.73010, 18.69629, 6.35766, 1.92111/15.02480, 6.21776, 1.57543/6.13126)
Br	(^2P)	(1333/233/3)	(34.73215, 19.29677, 6.61565, 2.08534/15.52028, 6.49953, 1.72266/6.49134)
Kr	(^1S)	(1333/233/3)	(35.73415, 19.89718, 6.87478, 2.24370/16.01548, 6.78257, 1.87065/6.84621)
Rb	(^2S)	(13333/233/3)	(36.73616, 20.50121, 7.13033, 2.46266, 0.62964/16.51154, 7.06560, 2.09696/7.19766)
Sr	(^1S)	(13333/233/3)	(37.73823, 21.10513, 7.38445, 2.67214, 0.78238/17.00734, 7.34749, 2.31165/7.54688)
Y	(^2D)	(13333/233/34)	(38.74074, 21.69777, 7.66717, 2.84457, 0.79996/17.49351, 7.65303, 2.47529/8.44236, 3.98864)
Zr	(^3F)	(13333/233/33)	(39.74268, 22.30418, 7.91441, 3.00048, 0.83244/17.99291, 7.92244, 2.62880/8.47561, 2.45682)
Nb	(^6D)	(12333/233/33)	(40.74475, 0.55741, 22.90709, 8.17268, 3.13958/18.48901, 8.19949, 2.76078/8.70942, 2.10832)
Mo	(^7S)	(12333/233/33)	(41.74690, 0.58744, 23.50913, 8.43118, 3.30298/18.98342, 8.47952, 2.92037/9.05368, 2.20192)
Tc	(^6S)	(13333/233/33)	(42.74906, 24.11146, 8.68479, 3.49111, 0.94060/19.47761, 8.75765, 3.10657/9.41985, 2.44649)
Ru	(^5F)	(12333/233/33)	(43.75124, 0.60412, 24.71237, 8.95102, 3.61853/19.97147, 9.03985, 3.23011/9.75000, 2.42998)
Rh	(^4F)	(12333/233/33)	(44.75343, 0.60829, 25.31378, 9.21182, 3.77064/20.46515, 9.31982, 3.37926/10.09936, 2.55712)
Pd	(^1S)	(13333/233/33)	(45.77610, 33.59288, 22.30693, 9.82317, 3.86366/20.96030, 9.60664, 3.49872/10.44740, 2.58951)

Table 2 (continued)

Atom		Principal quantum numbers	Exponents
Ag	(^2S)	(12333/233/33)	(46.75785, 0.61392, 26.51644, 9.73463, 4.06679/21.45195, 9.87931, 3.66969/10.79707, 2.81869)
Cd	(^1S)	(12333/233/33)	(47.76005, 0.75041, 27.11940, 9.98727, 4.23709, 21,94543, 10.15482, 3.84487/11.15010, 3.03561)
In	(^2P)	(13334/2333/33)	(48.76187, 27.72772, 10.30486, 1.25001, 5.51366/22.44001, 10.42879, 4.03674, 0.95529/11.50117, 3.24593)
Sn	(^3P)	(13334/2333/33)	(49.76395, 28.33207, 10.55953, 1.40143, 5.72749/22.93386, 10.70251, 4.22103, 1.10544/11.85015, 3.45263)
Sb	(^4S)	(13334/2333/33)	(50.76601, 28.93640, 10.81390, 1.53690, 5.94038/23.42756, 10.97549, 4.40506, 1.24685/12.19732, 3.65473)
Te	(^3P)	(13334/2333/33)	(51.76805, 29.54080, 11.06782, 1.66621, 6.15305/23.92102, 11.24761, 4.58972, 1.36315/12.54305, 3.85416)
I	(^2P)	(13334/2333/33)	(52.77007, 30.14519, 11.32143, 1.78831, 6.36519/24.41431, 11.51883, 4.77408, 1.48080/12.88738, 4.05069)
Xe	(^1S)	(13334/2333/33)	(53.77207, 30.74958, 11.57475, 1.90553, 6.57690/24.90737, 11.78912, 4.95779, 1.59691/13.23045, 4.24489)

particularly for $Z \geqslant 30$. The energies of the highest s-AOs in the 42 unconventional SZ functions have an average percent error, with respect to numerical Hartree–Fock values, of 8.12% to be compared with 16.68% for the conventional SZ functions. Similarly, the energies of the highest p-AOs in the unconventional SZ functions have an average error of 7.59% compared with 14.25% for the conventional SZ functions. The improvement in the valence p-AO energies is most noticeable in Fig. 1b for atoms in groups 13–18.

Table 3 shows that the energies of the highest d-AOs for the unconventional SZ functions are better than those for the conventional SZ functions except in the case of Sr. Our reoptimizations of the exponents of the conventional SZ functions did not remove the unphysical positive orbital energies for Cr, Cu, Zn, Y, Zr, and Pd. However, the unconventional SZ approximation does remove



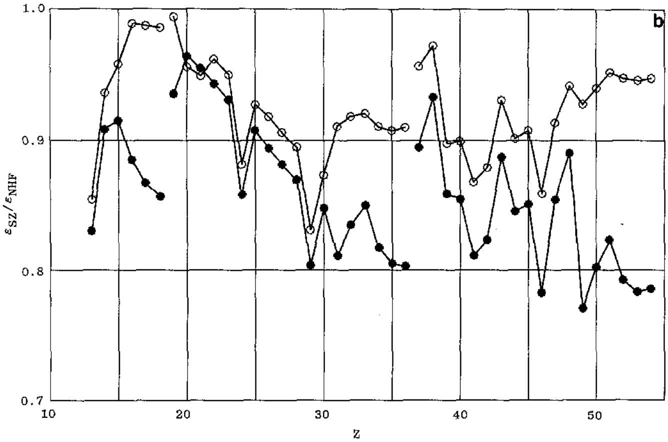


Fig. 1a,b. Comparison of the conventional (●) and our unconventional (○) SZ orbital energies ε_{SZ}. ε_{NHF} are numerical Hartree–Fock orbital energies. **a** highest *s*-orbitals, and **b** highest *p*-orbitals

Table 3. Comparison of the outermost *d* orbital energies

Atom		AO	Single-zeta		Numerical Hartree–Fock[a]
			Conventional	Present	
Sc	(^2D)	3*d*	−0.18990	−0.18489	−0.34371
Ti	(^3F)	3*d*	−0.24338	−0.29264	−0.44066
V	(^4F)	3*d*	−0.25641	−0.30833	−0.50962
Cr	(^7S)	3*d*	+0.02561	−0.02984	−0.32249
Mn	(^6S)	3*d*	−0.25165	−0.31056	−0.63885
Fe	(^5D)	3*d*	−0.15687	−0.22959	−0.64689
Co	(^4D)	3*d*	−0.08081	−0.15784	−0.67542
Ni	(^3F)	3*d*	−0.00051	−0.08201	−0.70693
Cu	(^2S)	3*d*	+0.50680	+0.43012	−0.49123
Zn	(^1S)	3*d*	+0.16629	+0.07537	−0.78254
Ga	(^2P)	3*d*	−0.24480	−0.36257	−1.19337
Ge	(^3P)	3*d*	−0.71576	−0.82401	−1.63490
As	(^4S)	3*d*	−1.21390	−1.21965	−2.11266
Se	(^3P)	3*d*	−1.75996	−1.76733	−2.64963
Br	(^2P)	3*d*	−2.33571	−2.34531	−3.22018
Kr	(^1S)	3*d*	−2.94300	−2.95537	−3.82523
Rb	(^2S)	3*d*	−3.87716	−3.88264	−4.73229
Sr	(^1S)	3*d*	−4.85927	−4.85727	−5.69439
Y	(^2D)	4*d*	+0.74249	+0.70769	−0.24985
Zr	(^3F)	4*d*	+0.00208	−0.09585	−0.33676
Nb	(^6D)	4*d*	−0.05598	−0.15383	−0.26766
Mo	(^7S)	4*d*	−0.10670	−0.21439	−0.31222
Tc	(^6S)	4*d*	−0.32152	−0.42416	−0.54395
Ru	(^5F)	4*d*	−0.09612	−0.23802	−0.40112
Rh	(^4F)	4*d*	−0.09904	−0.25859	−0.44602
Pd	(^1S)	4*d*	+0.18570	−0.02128	−0.33600
Ag	(^2S)	4*d*	−0.11319	−0.30962	−0.53739
Cd	(^1S)	4*d*	−0.38621	−0.58291	−0.76366
In	(^2P)	4*d*	−0.68967	−0.88763	−1.06314
Sn	(^3P)	4*d*	−1.02290	−1.21813	−1.36904
Sb	(^4S)	4*d*	−1.36129	−1.55564	−1.68787
Te	(^3P)	4*d*	−1.72179	−1.91746	−2.03829
I	(^2P)	4*d*	−2.09163	−2.29000	−2.40120
Xe	(^1S)	4*d*	−2.47298	−2.67530	−2.77788

[a] Refs [20] and [21]

them in Cr, Zr, and Pd. The energies of the highest d-AOs in the unconventional SZ functions have an average error of 56.1% compared with 71.5% for the conventional SZ functions. Unfortunately, even the optimal SZ approximation is rather poor for the d-orbitals. This confirms previous work [13, 22, 23] that d-type STFs are very poor representations of d-orbitals. Thus, one must either enlarge the d-block of the minimal STF basis set or use unconventional basis functions such as those suggested by Hojer [23].

4. Concluding remarks

We have found that the variational choice of the principal quantum numbers $\{n\}$ of the STFs improves remarkably the quality of a single-zeta or minimal STF basis set wave function. Compared to the conventional SZ function, the optimum SZ function lowers the atomic energy as much as 6.4 for Xe, for example. The improvement in the valence orbital energies is large, and some of the positive d orbital energies found in the conventional SZ calculation turn negative. It is satisfying that more stringent application of the variational principle improves the valence properties rather than worsens them at the expense of an improved core as conventional folklore would suggest.

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