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High-quality Gaussian basis sets for fourth-row atoms

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Summary. Energy-optimized Gaussian basis sets of triple-zeta quality for the atoms Rb–Xe have been derived. Two series of basis sets are developed; (24*s* 16*p* 10*d*) and (26*s* 16*p* 10*d*) sets which we expand to 13 *d* and 19 *p* functions as the 4*d* and 5*p* shells become occupied. For the atoms lighter than Cd, the (24*s* 16*p* 10*d*) sets with triple-zeta valence distributions are higher in energy than the corresponding double-zeta distribution. To ensure a triple-zeta distribution and a global energy minimum the (26*s* 16*p* 10*d*) sets were derived. Total atomic energies from the largest basis sets are between 198 and 284 μE_H above the numerical Hartree–Fock energies.

Key words: Gaussian basis sets, high-quality – Fourth-row atoms – Triple-zeta valence distribution

1 Introduction

Modern computational chemistry is to a large extent based on the use of finite basis sets of Gaussian-type orbitals (GTOs) for analytic expansion of one-particle functions. First introduced in quantum chemistry by Boys in 1950 [1], GTOs permit rapid evaluation of multicenter two-electron integrals, and for calculations on polyatomic molecules there is presently no practical alternative.

The chief disadvantage of GTO basis sets is that the functions give a poor representation of the region close to the atomic nucleus; thus for very accurate work a large number of basis functions are needed. While the integral evaluation time was a limiting factor in earlier work, the availability of more powerful computers and the development of efficient integral evaluation algorithms has reduced this limitation significantly. Today, in highly accurate work with an extensive treatment of electron correlation, the integral evaluation usually accounts for a relatively small fraction of the total computational effort. In addition, general contraction schemes, such as the recently developed atomic

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natural orbital (ANO) method [2], explicitly intended for use in correlated calculations, have eliminated much of the burden of handling large basis sets beyond the integral evaluation stage. At the same time, state-of-the-art calculations have reached the point where the lack of high-quality basis sets can be an obstacle for accurate studies [3–6].

For some time we have been involved in the development of high-quality energy optimized GTO basis [7–11]. In this work we extend these efforts to include sets of triple-zeta (TZ) quality – representing the main amplitude of each atomic orbital by at least three primitive GTO functions – for the fourth-row elements. Basis sets for all or groups of these elements have been derived previously by Faegri [11], Huzinaga [12], Hyla-Krispin et al. [13], and Gropen [14], and also special sets as the MINI and MIDI [15] and well-tempered sets [16] exist. However, since none of these are of TZ quality, the sets presented here are significantly more accurate. While relativistic effects become somewhat important for this row, their effect can to a large extent be accounted for through first order perturbation theory. Thus the basis sets presented in this work will principally be useful for nonrelativistic calculations where it is desirable to minimize the inaccuracies arising from the finite basis approximation. In addition, these basis sets, supplemented with additional compact functions, should be useful for high-quality relativistic calculations [17].

Although essentially all nonrelativistic calculations have employed a point charge for the nucleus, the finite size of the nucleus is possibly important for very heavy atoms. In this work we investigate the effect of nuclear size on the basis set and SCF energy of Xe and show that the energy gained by reoptimizing the exponents is insignificant for the size of the basis sets employed in this work.

2 Results and discussion

The details of our computational method and the strategies followed in energy optimizations of these basis sets have been described previously [7–9]. We have carried out pilot calculations on Ag and Xe to determine the size of basis set needed to obtain an energy balanced triple-zeta valence description. Unfortunately, with the size of basis required for a TZ valence distributions, we are faced with a problem of multiple energy minima. This has been discussed for the first-row transition-metal atoms [8] and manifests itself in two close-lying minima on the energy surface, each corresponding to a different distribution of orbital exponents. For Ag it was possible to find a (23*s* 15*p* 12*d*) basis set which had a TZ valence description, but this size of basis set did not support a TZ minimum for the elements lighter than Rh. Increasing the size to (24*s* 16*p* 13*d*), corresponding to (24*s* 16*p* 10*d*) for elements without occupied 4*d* orbitals, and (24*s* 19*p* 13*d*) for elements with occupied 5*p* orbitals, we are able to locate TZ minima for all atoms of the row except Rb, Sr, and Y. However, even for basis sets of this size, more energy is gained by improving the 4*s* description rather than providing a TZ 5*s*, and therefore distributions yielding a double-zeta 5*s* are lower in energy for the elements lighter than Cd.

To provide basis sets that ensure a TZ distribution and a global energy minimum, we have also derived (26*s* 16*p* 10*d*) sets supplemented by additional basis functions as the 4*d* and 5*p* shells become occupied. Thus, our largest set for Y is (26*s* 16*p* 13*d*) while the corresponding Xe set is (26*s* 19*p* 13*d*). For these sets the TZ distribution represents a stable, single minimum, with no competing DZ minimum nearby.

The problem with stabilizing the TZ distribution also influences the choice of atomic state used in the optimization of the basis sets. The states derived from the orbital occupations $5s^24d^n$, $5s^14d^{n+1}$, and $5s^04d^{n+2}$ are close in energy for the transition metal atoms of the fourth row and only Y, Zr, Tc, and Cd have a $5s^24d^n$ ground state configuration. Pd has $5s^04d^{n+2}$, while Nb, Mo, Ru, Rh, and Ag have $5s^14d^{n+1}$ ground states. For transition-metal atoms, rather than using the ground states, we have chosen to use the lowest $5s^24d^n$ states for the orbital exponent optimizations as this stabilizes the TZ distribution for the 5*s* shell – with more 5*s* electrons the contribution to the total electronic energy from this shell increases, making an optimal description of the 5*s* orbital important. Also, previous experience with calculations involving transition metal atoms has shown that the basis sets optimized for the lowest s^2d^n state, supplemented with suitable diffuse functions, yield a balanced description of the low-lying states [18], and provide a good starting point for molecular calculations where states derived from several of these occupations interact.

The energies obtained with the various basis sets are listed in Table 1, where we also give a comparison with the numerical Hartree–Fock (NHF) results. All energies calculated with the basis sets containing 24 *s* functions are within 400 μE_H of the numerical results, while the 26 *s* sets have a maximum deviation of 284 μE_H (for Cd) and for most sets are within 250 μE_H of the NHF results. The apparently discontinuous improvement in quality between Cd and In is due to the addition of three *p* functions which not only describe the 5*p* shell, but also improve the description of the inner *p* shells. Supplementary functions were also optimized to describe Rb (^2P), Sr (^3P), and I^- (^1S). However, the energy improvement over employing even-tempered diffuse functions (ratio of 2.5) is insignificant. For the transition-metal atoms, previous experience has shown that adding an even-tempered *d* and three even-tempered *p* functions is adequate [10, 18].

As noted in the introduction, a possible problem with calculations using very large basis sets for heavy atoms is the finite size of the nucleus. While most quantum chemical calculations are based on point-charge nuclei, the finite size of the nucleus should be accounted for in accurate calculations on heavy atoms. A simple model for finite size nuclei that has been successfully employed in relativistic calculations is a charge distribution represented by a single Gaussian [19]. Calculations based on a Fermi distribution suggest that the exponent for this Gaussian nuclear charge distribution should be approximately 1.8×10^8 for Xe. Considering that the highest *s*-orbital exponent for the Xe (26*s* 19*p* 13*d*) set is 1.7×10^8, the point nucleus basis set contains at least one function that is almost entirely within the nuclear region.

The main effect of the finite nuclear size is to raise the total electronic energy of the atom, due to reduced nuclear attraction. This in itself need not affect chemical calculations significantly, as the changes induced in the low-lying core orbitals – mainly 1*s* – have a marginal effect on the valence orbitals. To investigate the importance of using a finite nucleus, we have optimized Xe basis sets ranging from (20*s* 12*p* 7*d*) to (25*s* 12*p* 7*d*) both for the point nucleus and for the Gaussian charge distribution (GCD). The energy increase due to the finite nuclear size of Xe is 103.6 $\mathrm{m}E_H$ (constant for all basis sets) out of a total energy of almost $-7232\, E_H$. Employing the finite nucleus pushes the 1*s* orbitals outwards compared to the point charge, causing the optimal values of the 1*s* exponents to increase more rapidly for point nuclei than for the GCD. In Fig. 1, a plot of the ratios of the exponents optimized using the point nucleus and the

Table 1. Atomic energies for fourth-row atoms from numerical Hartree–Fock (NHF) and finite basis (GTO) calculations in hartree units (E_H), and their difference (Δ) in μE_H. DZ (TZ) – double (triple) zeta for 5*s* shell

Atom	NHF energy	Basis	GTO energy	Δ
Rb (^2S)	−2938.357457	24,16,10 DZ	−0.357225	232
		26,16,10	−0.357254	203
Sr (^1S)	−3131.545689	24,16,10 DZ	−0.545457	232
		26,16,10	−0.545491	198
Y (^2D)	−3331.684169	24,16,13 DZ	−0.683920	249
		26,16,13	−0.683964	205
Zr (^3F)	−3538.995065	24,16,13 DZ	−0.994805	260
		24,16,13 TZ	−0.994784	281
		26,16,13	−0.994855	210
Nb (^4F)	−3753.552031	24,16,13 DZ	−0.551759	272
		24,16,13 TZ	−0.551742	289
		26,16,13	−0.551816	215
Mo (^5D)	−3975.443320	24,16,13 DZ	−0.443036	284
		24,16,13 TZ	−0.443022	298
		26,16,13	−0.443098	222
Tc (^6S)	−4204.788736	24,16,13 DZ	−0.788442	294
		24,16,13 TZ	−0.788431	305
		26,16,13	−0.788509	227
Ru (^5D)	−4441.487348	24,16,13 DZ	−0.487032	316
		24,16,13 TZ	−0.487026	322
		26,16,13	−0.487105	243
Rh (^4F)	−4685.801249	24,16,13 DZ	−0.800916	333
		24,16,13 TZ	−0.800914	335
		26,16,13	−0.800996	253
Pd (^3F)	−4937.783027	24,16,13 DZ	−0.782677	350
		24,16,13 TZ	−0.782679	348
		26,16,13	−0.782764	263
Ag (^2D)	−5197.517887	24,16,13 DZ	−0.517520	367
		24,16,13 TZ	−0.517526	361
		26,16,13	−0.517613	274
Cd (^1S)	−5465.133142	24,16,13 DZ	−0.132758	384
		24,16,13 TZ	−0.132768	374
		26,16,13	−0.132858	284
In (^2P)	−5740.169155	24,19,13 DZ	−0.168834	321
		24,19,13 TZ	−0.168848	307
		26,19,13	−0.168938	217
Sn (^3P)	−6022.931695	24,19,13 TZ	−0.931397	298
		26,19,13	−0.931486	209
Sb (^4S)	−6313.485321	24,19,13 TZ	−0.485029	292
		26,19,13	−0.485117	204
Te (^3P)	−6611.784059	24,19,13 TZ	−0.783821	297
		26,19,13	−0.783850	209
I (^2P)	−6917.980895	24,19,13 TZ	−0.980596	299
		26,19,13	−0.980685	210
Xe (^1S)	−7232.138365	24,19,13 TZ	−0.138065	300
		26,19,13	−0.138154	211

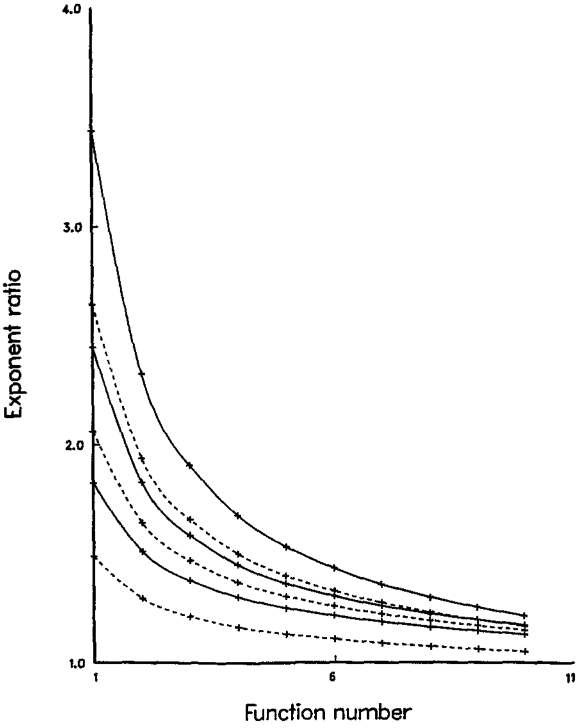

Fig. 1. The ratio between orbital exponents from basis sets optimized for a point nucleus and for a Gaussian finite nuclear charge distribution (GCD), respectively. The plot shows $R_i = \zeta(point)_i/\zeta(\mathrm{GCD})_i$ ($i = 1, 2, \ldots, 10$) for Xe sets (20*s* 12*p* 7*d*) to (25*s* 12*p* 7*d*) from bottom to top. *Broken line*: curves for (20*s* 12*p* 7*d*), (22*s* 12*p* 7*d*), and (24*s* 12*p* 7*d*)

GCD for the various sets clearly shows how the finite nucleus keeps the exponents smaller. However, for the size of basis sets considered here, the energy gained from reoptimizing the point-nucleus basis sets for a GCD nucleus is insignificant; ranging from 63 μE_H for the (20*s* 12*p* 7*d*) sets to 19 μE_H for the (25*s* 12*p* 7*d*) set. An interesting feature of basis sets optimized for a finite-sized nucleus is that the ratio between the two largest *s* orbital exponents is no longer constant, which is the case for point-nucleus basis sets. Thus, for Xe this ratio is an almost constant 6.69 using a point nucleus, whereas it varies from 5.82 to 4.51 for the GCD basis sets.

3 Conclusions

Energy-optimized high-quality GTO basis sets have been presented for the fourth-row atoms, Rb to Xe. The largest sets have a TZ valence distribution and are within 284 μE_H of the NHF energy. Employing a finite-size nucleus is shown to raise the energy slightly compared to employing a point charge, and to push the core orbitals outwards. However, the energy gain from reoptimizing the exponents from a point-charge nucleus basis set is insignificant. All of the basis sets optimized in this work are available from QCPE [20] and as a NASA technical report [21].

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