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Validity of *B*-splines as a universal basis set for atomic Hartree–Fock–Roothaan calculations

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Abstract. The validity of *B*-splines as a universal basis set for atomic Hartree–Fock–Roothaan calculations is studied. In order to accomplish our aim, the ground-state energies of neutral atoms He–Xe, cations Li^{+}–Xe^{+}, and anions H^{-}–I^{-} with the nuclear charge $Z \leq 54$ are calculated by the Hartree–Fock–Roothaan method with the *B*-spline sets. All radial functions of the atoms and singly charged ions are expanded by common *B*-spline sets regardless of atomic systems and symmetries of atomic orbitals. The energies obtained by the best *B*-spline set are in excellent agreement with ten-digit numerical Hartree–Fock results.

Keywords: *B*-splines – Hartree–Fock–Roothaan – Universal basis set – He–Xe – H^{-}–I^{-}

1 Introduction

Atomic Hartree–Fock equations are solved usually by two methods, that is, a numerical method and an analytic method. A numerical Hartree–Fock (NHF) method has been formulated by Froese Fischer [1], and it can give very accurate results. On the other hand, an analytic Hartree–Fock method has been developed by Roothaan [2] using the Rayleigh–Ritz variational procedure, and is often called the Hartree–Fock–Roothaan (HFR) method. The HFR method can be applied to polyatomic molecules because wave functions are represented as basis set expansions. As the basis set, Slater-type functions (STFs) or Gaussian-type functions (GTFs) are usually employed; however, before the actual application of the HFR method, optimization of their nonlinear parameters (i.e., exponents), which is laborious and tedious work, has to be carried out.

Clementi and Roetti [4] published a monumental compilation of atomic HFR wave functions calculated with fully optimized STFs in 1974. It is known that their calculations include some errors compared to the NHF results. Tatewaki and Sekiya [5] and Bunge et al. [6] have improved the results of Clementi and Roetti by employing optimal STF principal quantum numbers in addition to optimizing the exponents.

Some methods to reduce the load needed for the optimization of STF and GTF exponents have been proposed and applied extensively. The simplest method would be the even-tempering scheme proposed by Raffenetti [7]. The even-tempering method generates the exponents for each symmetry by two parameters through a geometric sequence. An interesting application of the even-tempering method has been performed by Koga et al. [8]. They employed two independent geometric sequences for generating STF exponents in each symmetry. Their method is called the double even-tempering scheme. Huzinaga and coworkers [9] have further extended the even-tempering method to a more complicated procedure with four parameters; this is called the well-tempering method. As far as we know, this well-tempering method has been applied to GTFs only.

In addition to STFs and GTFs, piecewise polynomials can be used in practical calculations. The piecewise polynomials were introduced to atomic calculations by Gilbert and coworkers [11,12]. Their use has been further developed by the group of Silverstone [13,14,15]. Especially, *B*-splines have been used for atomic calculations recently. The first application of the *B*-splines to atomic calculations was carried out by Shore [16]. It has been further applied to atomic Dirac and Hartree-Fock equations with the Galerkin procedure by Bottcher and Strayer [17], Johnson and coworkers [18,19], Froese Fischer and coworkers [20,21], and others. In addition, Jeng and Hsue [22] have carried out atomic relativistic density functional calculations with the *B*-splines.

The *B*-splines are flexible and free from computational linear dependence. The flexibility of the *B*-splines

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will make it possible to apply a common B-spline set to all atoms irrespective of orbital symmetry without loss of accuracy. Consequently, the B-spline set can be a candidate for a universal basis set. Moreover, this universality will make it possible to store all atomic integrals over the B-splines so that they can be used for various atomic calculations. In the present work, we studied the validity of the B-splines as a universal basis set. In order to accomplish our aim, we applied the B-spline sets to the HFR calculations of the ground states of neutral atoms He–Xe, cations Li^+–Xe^+, and anions H^-–I^- with the nuclear charge $Z \le 54$, and compared their energies with the ten-digit NHF energies obtained by Koga and coworkers [23,24].

In the next section, we explain the details of the B-spline HFR calculations for the atomic systems. The results and discussions are given in the third section. Hartree atomic units are used throughout.

2 Computational method

The B-splines of order K are piecewise polynomials of degree $K-1$ on a knot sequence in a cavity of radius R. The knot sequence is a set of points defined on a interval $[0,R]$. To construct a set of M B-splines, the knot sequence has to be generated in $[0,R]$. The quality of the B-spline set depends not only on the order and size, but also on the knot sequence; hence, the way to generate the knot sequence is important. Several procedures to generate the knot sequence have been proposed by Gilbert and Bertoncini [11]. In the present work, to obtain a concentration of the knots near the nucleus where atomic orbitals are changing rapidly, we employed the knot sequence with K-fold multiplicity $\{t_i\}$ $(i = 1, 2, \ldots, M+K)$:

$$t_i = \begin{cases} 0, & i = 1, \ldots, K \\ R_1 \sum_{j=1}^{i-K} \alpha^{j-1}, & i = K+1, \ldots, M \\ R, & i = M+1, \ldots, M+K \end{cases} , \tag{1}$$

where R_1 is the initial point and α is a parameter to specify the distribution of the knots. α is chosen to satisfy the following equation:

$$R = R_1(1 + \alpha + \alpha^2 + \cdots + \alpha^{M-K}) \ . \tag{2}$$

The B-splines of order K, $\{B_{i,K}(r)\}$, are constructed recursively by de Boor–Cox relations [10] :

$$B_{i,1}(r) = \begin{cases} 1, & t_i \le r < t_{i+1} \\ 0, & \text{otherwise} \end{cases} \tag{3}$$

and

$$B_{i,K}(r) = \frac{r - t_i}{t_{i+K-1} - t_i} B_{i,K-1}(r) + \frac{t_{i+K} - r}{t_{i+K} - t_{i+1}} B_{i+1,K-1}(r) \ . \tag{4}$$

Thus, $B_{i,K}(r)$ is $K-1$ degree polynomials of r. $B_{i,K}(r)$ is nonzero in $t_i \le r < t_{i+K}$. The first derivative of $B_{i,K}(r)$, $B'_{i,K}(r)$, is calculated by the formula

$$B'_{i,K}(r) = (K-1)\left[\frac{B_{i,K-1}(r)}{t_{i+K-1} - t_i} - \frac{B_{i+1,K-1}(r)}{t_{i+K} - t_{i+1}}\right] \tag{5}$$

with Eqs.(3) and (4).

We expand the radial function $P_{n\lambda}(r)$ of the atomic orbital with symmetry λ

$$\psi_{n\lambda m}(r, \theta, \varphi) = r^{-1} P_{n\lambda}(r) Y_\lambda^m(\theta, \varphi) \tag{6}$$

by the B-splines and enforce the boundary conditions $P_{n\lambda}(0) = 0$ and $P_{n\lambda}(R) = 0$. Since the first and last terms of the B-splines with K-fold multiple knots are nonzero at $r = 0$ and at $r = R$, respectively, we remove them from the basis set to satisfy the boundary conditions. Namely, the radial function $P_{n\lambda}(r)$ is expanded as

$$P_{n\lambda}(r) = \sum_{i=1}^{N} C_{n\lambda,i} B_{i+1,K}(r) \ , \tag{7}$$

where N is the number of the B-splines used in the HFR calculations, i.e., $N = M - 2$. We use the same basis set regardless of atomic systems and symmetries of their orbitals.

All the integrals needed in HFR calculations are evaluated by the Gauss integration procedure. The one-electron overlap, kinetic, and nuclear attraction integrals are

$$S_{ij} = \int_0^R \mathrm{d}r B_{i,K}(r) B_{j,K}(r) \ , \tag{8}$$

$$T_{ij} = \frac{1}{2} \int_0^R \mathrm{d}r \Big[B'_{i,K}(r) B'_{j,K}(r). + \lambda(\lambda+1) r^{-2} B_{i,K}(r) B_{j,K}(r) \Big] \ , \tag{9}$$

and

$$V_{ij} = \int_0^R \mathrm{d}r r^{-1} B_{i,K}(r) B_{j,K}(r) \ , \tag{10}$$

respectively. Evaluation of $\frac{1}{2}N(N+1)$ one-electron integrals (OEIs) is needed in usual HFR calculations [3]; however, the number of OEIs, N_{OEI}, needed in the B-spline HFR calculations is less than $\frac{1}{2}N(N+1)$ because products $B_{i,K}(r)B_{j,K}(r)$ $(i \ge j)$ vanish outside the region $t_i \le r < t_{j+K}$ owing to the definition of the B-splines. Hence, only OEIs which satisfy the conditions $i - j < K$ and $i \ge j$ have to be evaluated. Therefore,

$$N_{\mathrm{OEI}} = \frac{1}{2} K(2N - K + 1) \ . \tag{11}$$

The supermatrices $P_{\lambda ij,\mu kl}$ and $Q_{\lambda ij,\mu kl}$ defined by Roothaan and Bagus [3] are rewritten by using two-electron integrals (TEIs)

$$R^{\nu}_{ij,kl} = \int_0^R \mathrm{d}r_1 \int_0^R \mathrm{d}r_2 B_{i,K}(r_1) B_{j,K}(r_1) \times \frac{r_<^{\nu}}{r_>^{\nu+1}} B_{k,K}(r_2) B_{l,K}(r_2) \tag{12}$$

as follows :

$$P_{\lambda ij,\mu kl} = R^0_{ij,kl} - \frac{1}{2}\sum_{v=|\lambda-\mu|}^{\lambda+\mu} A_{\lambda\mu v} R^v_{ik,jl} \tag{13}$$

and

$$Q_{\lambda ij,\mu kl} = \sum_{v=0}^{2(\lambda,\mu)_<} J_{\lambda\mu v} R^v_{ij,kl} - \frac{1}{2}\sum_{v=|\lambda-\mu|}^{\lambda+\mu} K_{\lambda\mu v} R^v_{ik,jl} \ , \tag{14}$$

where $A_{\lambda\mu v}$, $J_{\lambda\mu v}$, and $K_{\lambda\mu v}$ are numerical coefficients [3,25]. Since the supermatrices contain redundant TEIs, we have to evaluate only the distinct nonzero TEIs, which satisfy the conditions $i - j < K$, $k - l < K$, $i \geq j$, $k \geq l$, and $\frac{1}{2}i(i-1) + j \geq \frac{1}{2}k(k-1) + l$. The last three conditions arise from the permutational symmetries of indices i, j, k, and l of TEIs. The number of TEIs, N_{TEI}, needed for the construction of the supermatrices finally becomes

$$N_{\mathrm{TEI}} = \frac{1}{2} N_{\mathrm{OEI}}(N_{\mathrm{OEI}} + 1)(2\lambda_{\max} + 1) \ , \tag{15}$$

where $\lambda_{\max}$ is the maximum azimuthal quantum number of an atom under consideration.

The parameters of the B-spline sets employed in the present HFR calculations are summarized in Table 1. The maximum value of R was 40 for the neutral atoms and cations. For the anions, we employed $R = 40$, 50, and 60 because of the diffuse character of their orbitals. The basis set with small K cannot give an accurate description of the orbitals near the nucleus unless the knots near the nucleus are sufficiently close together. Hence, we should use smaller R_1 for small K. Hereafter, we denote a set of B-splines specified by K, N, and R as $\mathscr{B}^K_{N,R}$ to simplify the notation.

All the HFR calculations with the B-splines were carried out by our atomic self-consistent-field program code based on the algorithm of Roothaan and Bagus [3].

3 Results and discussions

We calculated the B-spline HFR energies for all the atomic systems using a personal computer (AMD Duron 1GHz) and obtained ten-digit results. Although there are many integrals, it is possible to reduce the computational amount by storing all the integrals over a common B-spline set throughout the calculations. The calculated virial ratios were in agreement to within 7–10 digits of the exact value for all the cases. For the neutral atoms and cations, the errors of the virial ratios decreased with increasing order or size of the B-splines. All the virial ratios calculated with $\mathscr{B}^9_{40,40}$ were in perfect agreement to within ten-digits of the exact value. The virial ratio errors for the anions decreased with increasing R owing to the diffuse character of their orbitals.

We have summarized the deviations of the B-spline HFR energies from the ten-digit NHF results for the neutral atoms [23] in Table 2. The energy deviations increase with increasing Z. This tendency is obvious for the basis sets with smaller K. In addition, Table 2 indicates that the quality of the B-spline sets depends on K. For example, $\mathscr{B}^5_{30,30}$ yields an energy deviation for Xe 165 times larger than $\mathscr{B}^9_{30,30}$; however, the energy deviation of Xe decreases with increasing K. When N and R are large, even the B-spline sets with small K give accurate results for the neutral atoms. In fact, one can see from Table 2 that the quality of $\mathscr{B}^5_{40,40}$ equals that of $\mathscr{B}^6_{30,30}$. Similarly, $\mathscr{B}^6_{40,40}$ also has the same equality as $\mathscr{B}^9_{30,30}$. The smallest basis set in the present work, $\mathscr{B}^9_{25,25}$, gives comparable results as $\mathscr{B}^6_{30,30}$ and $\mathscr{B}^5_{40,40}$ up to the third-row atoms. $\mathscr{B}^7_{40,40}$, of which K, N, and R are larger, gives very accurate HFR energies. Although the results are not shown in Table 2, the HFR energies given by $\mathscr{B}^9_{40,40}$ are in perfect agreement with the ten-digit NHF values. Hence, $\mathscr{B}^9_{40,40}$ can be used as a universal basis set for the neutral atoms.

In addition to the neutral atoms, we calculated the B-spline HFR energies of the cations. Since the parameter dependence of the cation total energies is parallel to that of the neutral cases listed in Table 2, we have not shown their values. It is found that the basis sets for the neutral atoms are applicable to the cations without sacrificing the total energy because electron distributions of the cations are more compact than those of the neutral atoms. Therefore, $\mathscr{B}^9_{40,40}$ can be also used as a universal basis set for the cations as well as the neutral atoms.

Table 1. Parameters of B-spline sets

Neutral atoms and cations					Anions				
N	R	K	R_1	Notation	N	R	K	R_1	Notation
25	25	9	0.020	$\mathscr{B}^9_{25,25}$	40	40	7	0.008	$\mathscr{B}^7_{40,40}$
							9	0.010	$\mathscr{B}^9_{40,40}$
30	30	5	0.005	$\mathscr{B}^5_{30,30}$					
		6	0.007	$\mathscr{B}^6_{30,30}$	40	50	7	0.008	$\mathscr{B}^7_{40,50}$
		7	0.009	$\mathscr{B}^7_{30,30}$			9	0.010	$\mathscr{B}^9_{40,50}$
		9	0.014	$\mathscr{B}^9_{30,30}$					
					40	60	7	0.008	$\mathscr{B}^7_{40,60}$
40	40	5	0.004	$\mathscr{B}^5_{40,40}$			9	0.010	$\mathscr{B}^9_{40,60}$
		6	0.005	$\mathscr{B}^6_{40,40}$					
		7	0.008	$\mathscr{B}^7_{40,40}$					
		9	0.010	$\mathscr{B}^9_{40,40}$					

Table 2. Deviations of the *B*-spline Hartree–Fock–Roothaan (HFR) energies from the ten-digit numerical Hartree–Fock (NHF) results for the neutral atoms (μ hartree)

Z	Atom	Configuration	State	$N, R = 25$	$N, R = 30$				$N, R = 40^{\mathrm{a}}$			NHF [23]
				$K = 9$ $\mathscr{B}^{9}_{25,25}$	$K = 5$ $\mathscr{B}^{5}_{30,30}$	$K = 6$ $\mathscr{B}^{6}_{30,30}$	$K = 7$ $\mathscr{B}^{7}_{30,30}$	$K = 9$ $\mathscr{B}^{9}_{30,30}$	$K = 5$ $\mathscr{B}^{5}_{40,40}$	$K = 6$ $\mathscr{B}^{6}_{40,40}$	$K = 7$ $\mathscr{B}^{7}_{40,40}$	
2	He	$1s^{2}$	$^{1}\mathrm{S}$	0.001	0.046	0.003	0.001	0.000	0.005	0.001	0.000	−2.861679996
3	Li	$[\mathrm{He}]2s^{1}$	$^{2}\mathrm{S}$	0.003	0.172	0.010	0.001	0.000	0.016	0.001	0.000	−7.432726931
4	Be	$[\mathrm{He}]2s^{2}$	$^{1}\mathrm{S}$	0.01	0.40	0.02	0.00	0.00	0.04	0.00	0.00	−14.57302317
5	B	$[\mathrm{He}]2s^{2}2p^{1}$	$^{2}\mathrm{P}$	0.01	0.72	0.04	0.01	0.00	0.07	0.00	0.00	−24.52906073
6	C	$[\mathrm{He}]2s^{2}2p^{2}$	$^{3}\mathrm{P}$	0.02	1.16	0.07	0.00	0.00	0.11	0.00	0.00	−37.68861896
7	N	$[\mathrm{He}]2s^{2}2p^{3}$	$^{4}\mathrm{S}$	0.03	1.74	0.11	0.01	0.00	0.16	0.01	0.00	−54.40093421
8	O	$[\mathrm{He}]2s^{2}2p^{4}$	$^{3}\mathrm{P}$	0.04	2.45	0.15	0.02	0.00	0.23	0.01	0.00	−74.80939847
9	F	$[\mathrm{He}]2s^{2}2p^{5}$	$^{2}\mathrm{P}$	0.06	3.33	0.21	0.03	0.00	0.32	0.01	0.00	−99.40934939
10	Ne	$[\mathrm{He}]2s^{2}2p^{6}$	$^{1}\mathrm{S}$	0.1	4.4	0.3	0.0	0.0	0.4	0.0	0.0	−128.5470981
11	Na	$[\mathrm{Ne}]3s^{1}$	$^{2}\mathrm{S}$	0.1	5.9	0.4	0.0	0.0	0.5	0.0	0.0	−161.8589116
12	Mg	$[\mathrm{Ne}]3s^{2}$	$^{1}\mathrm{S}$	0.2	7.9	0.5	0.0	0.0	0.7	0.0	0.0	−199.6146364
13	Al	$[\mathrm{Ne}]3s^{2}3p^{1}$	$^{2}\mathrm{P}$	0.3	10.5	0.7	0.1	0.1	1.0	0.1	0.0	−241.8767073
14	Si	$[\mathrm{Ne}]3s^{2}3p^{2}$	$^{3}\mathrm{P}$	0.5	13.6	0.9	0.1	0.0	1.3	0.0	0.0	−288.8543625
15	P	$[\mathrm{Ne}]3s^{2}3p^{3}$	$^{4}\mathrm{S}$	0.6	17.5	1.2	0.2	0.0	1.7	0.1	0.0	−340.7187810
16	S	$[\mathrm{Ne}]3s^{2}3p^{4}$	$^{3}\mathrm{P}$	0.9	22.0	1.5	0.2	0.0	2.0	0.1	0.0	−397.5048959
17	Cl	$[\mathrm{Ne}]3s^{2}3p^{5}$	$^{2}\mathrm{P}$	1.4	27.4	2.0	0.3	0.0	2.5	0.1	0.0	−459.4820724
18	Ar	$[\mathrm{Ne}]3s^{2}3p^{6}$	$^{1}\mathrm{S}$	1.8	33.7	2.5	0.3	0.0	3.1	0.1	0.0	−526.8175128
19	K	$[\mathrm{Ar}]4s^{1}$	$^{2}\mathrm{S}$	2.2	41.6	3.2	0.5	0.1	3.9	0.2	0.0	−599.1647868
20	Ca	$[\mathrm{Ar}]4s^{2}$	$^{1}\mathrm{S}$	3.2	51.1	3.9	0.5	0.0	4.7	0.2	0.0	−676.7581859
21	Sc	$[\mathrm{Ar}]4s^{2}3d^{1}$	$^{2}\mathrm{D}$	4.5	60.7	4.7	0.6	0.0	5.5	0.2	0.0	−759.7357180
22	Ti	$[\mathrm{Ar}]4s^{2}3d^{2}$	$^{3}\mathrm{F}$	5.8	71.2	5.6	0.8	0.1	6.5	0.3	0.0	−848.4059970
23	V	$[\mathrm{Ar}]4s^{2}3d^{3}$	$^{4}\mathrm{F}$	6.3	82.6	6.6	0.9	0.1	7.5	0.3	0.0	−942.8843377
24	Cr	$[\mathrm{Ar}]4s^{1}3d^{5}$	$^{7}\mathrm{S}$	6	94	7	1	0	8	0	0	−1043.356376
25	Mn	$[\mathrm{Ar}]4s^{2}3d^{5}$	$^{6}\mathrm{S}$	8	109	9	2	0	10	1	0	−1149.866252
26	Fe	$[\mathrm{Ar}]4s^{2}3d^{6}$	$^{5}\mathrm{D}$	10	123	10	1	0	11	0	0	−1262.443665
27	Co	$[\mathrm{Ar}]4s^{2}3d^{7}$	$^{4}\mathrm{F}$	14	140	12	2	0	13	1	0	−1381.414553
28	Ni	$[\mathrm{Ar}]4s^{2}3d^{8}$	$^{3}\mathrm{F}$	18	158	13	2	0	14	0	0	−1506.870908
29	Cu	$[\mathrm{Ar}]4s^{1}3d^{10}$	$^{2}\mathrm{S}$	20	175	15	2	0	16	1	0	−1638.963742
30	Zn	$[\mathrm{Ar}]4s^{2}3d^{10}$	$^{1}\mathrm{S}$	21	197	17	2	0	18	1	0	−1777.848116
31	Ga	$[\mathrm{Ar}]4s^{2}3d^{10}4p^{1}$	$^{2}\mathrm{P}$	23	222	20	3	1	21	1	0	−1923.261010
32	Ge	$[\mathrm{Ar}]4s^{2}3d^{10}4p^{2}$	$^{3}\mathrm{P}$	24	249	22	4	1	23	1	0	−2075.359734
33	As	$[\mathrm{Ar}]4s^{2}3d^{10}4p^{3}$	$^{4}\mathrm{S}$	28	278	25	4	0	26	1	0	−2234.238654
34	Se	$[\mathrm{Ar}]4s^{2}3d^{10}4p^{4}$	$^{3}\mathrm{P}$	35	312	29	5	1	29	2	0	−2399.867612
35	Br	$[\mathrm{Ar}]4s^{2}3d^{10}4p^{5}$	$^{2}\mathrm{P}$	46	349	32	5	1	32	1	0	−2572.441333
36	Kr	$[\mathrm{Ar}]4s^{2}3d^{10}4p^{6}$	$^{1}\mathrm{S}$	62	390	36	6	1	36	1	0	−2752.054977
37	Rb	$[\mathrm{Kr}]5s^{1}$	$^{2}\mathrm{S}$	81	436	41	7	1	41	2	0	−2938.357454
38	Sr	$[\mathrm{Kr}]5s^{2}$	$^{1}\mathrm{S}$	102	487	46	7	1	45	2	0	−3131.545686
39	Y	$[\mathrm{Kr}]5s^{2}4d^{1}$	$^{2}\mathrm{D}$	119	543	52	9	2	51	3	0	−3331.684170
40	Zr	$[\mathrm{Kr}]5s^{2}4d^{2}$	$^{3}\mathrm{F}$	128	603	59	10	2	57	3	0	−3538.995065
41	Nb	$[\mathrm{Kr}]5s^{1}4d^{4}$	$^{6}\mathrm{D}$	128	666	65	12	3	63	3	0	−3753.597728
42	Mo	$[\mathrm{Kr}]5s^{1}4d^{5}$	$^{7}\mathrm{S}$	124	735	73	13	3	69	4	1	−3975.549500
43	Tc	$[\mathrm{Kr}]5s^{2}4d^{5}$	$^{6}\mathrm{S}$	121	813	82	15	3	76	4	0	−4204.788737
44	Ru	$[\mathrm{Kr}]5s^{1}4d^{7}$	$^{5}\mathrm{F}$	133	892	91	17	4	84	4	1	−4441.539488
45	Rh	$[\mathrm{Kr}]5s^{1}4d^{8}$	$^{4}\mathrm{F}$	165	979	101	18	4	92	4	0	−4685.881704
46	Pd	$[\mathrm{Kr}]4d^{10}$	$^{1}\mathrm{S}$	221	1071	112	21	5	100	5	0	−4937.921024
47	Ag	$[\mathrm{Kr}]5s^{1}4d^{10}$	$^{2}\mathrm{S}$	299	1174	124	23	6	110	5	0	−5197.698473
48	Cd	$[\mathrm{Kr}]5s^{2}4d^{10}$	$^{1}\mathrm{S}$	391	1288	138	27	8	121	7	1	−5465.133143
49	In	$[\mathrm{Kr}]5s^{2}4d^{10}5p^{1}$	$^{2}\mathrm{P}$	484	1410	153	30	9	133	7	1	−5740.169156
50	Sn	$[\mathrm{Kr}]5s^{2}4d^{10}5p^{2}$	$^{3}\mathrm{P}$	564	1543	168	33	10	145	7	0	−6022.931695
51	Sb	$[\mathrm{Kr}]5s^{2}4d^{10}5p^{3}$	$^{4}\mathrm{S}$	624	1688	186	38	12	159	8	1	−6313.485321
52	Te	$[\mathrm{Kr}]5s^{2}4d^{10}5p^{4}$	$^{3}\mathrm{P}$	663	1844	205	41	12	173	9	1	−6611.784059
53	I	$[\mathrm{Kr}]5s^{2}4d^{10}5p^{5}$	$^{2}\mathrm{P}$	693	2014	227	46	13	189	10	1	−6917.980896
54	Xe	$[\mathrm{Kr}]5s^{2}4d^{10}5p^{6}$	$^{1}\mathrm{S}$	736	2199	252	51	13	207	11	1	−7232.138364

[a] Results for $K = 9$ exactly coincide with the NHF values

In Table 3, we have summarized the deviations of the *B*-spline HFR energies from the ten-digit NHF results for the anions [24]. An application of $\mathscr{B}^{9}_{40,40}$ to the anions causes some energy deviations, as seen from Table 3. In particular, for the alkali-metal anions and Y^{-}, the energy deviations are quite large owing to the existence of loosely bound electrons in the outermost orbitals. However, the energy deviations do not depend on K. This implies that our *B*-spline size N is sufficient for the anions. Since the outermost orbitals of the anions are more diffuse than those of the neutral atoms, the energy deviations decrease with increasing R. Consequently, the

Table 3. Deviations of the *B*-spline HFR energies from the ten-digit NHF results for the anions (μ hartree)

Z	Atom	Configuration	State	$N = 40, R = 40$		$N = 40, R = 50$		$N = 40, R = 60$		NHF [24]
				$K = 7$ $\mathscr{B}^7_{40,40}$	$K = 9$ $\mathscr{B}^9_{40,40}$	$K = 7$ $\mathscr{B}^7_{40,50}$	$K = 9$ $\mathscr{B}^9_{40,50}$	$K = 7$ $\mathscr{B}^7_{40,60}$	$K = 9$ $\mathscr{B}^9_{40,60}$	
1	H^-	$1s^2$	^1S	0.000	0.000	0.000	0.000	0.000	0.000	−0.487929734
3	Li^-	$[He]2s^2$	^1S	0.420	0.420	0.014	0.014	0.001	0.000	−7.428232061
5	B^-	$[He]2s^2 2p^2$	^3P	0.00	0.00	0.00	0.00	0.00	0.00	−24.51922137
6	C^-	$[He]2s^2 2p^3$	^4S	0.00	0.00	0.00	0.00	0.00	0.00	−37.70884362
7	N^-	$[He]2s^2 2p^4$	^3P	0.00	0.00	0.00	0.00	0.00	0.00	−54.32195889
8	O^-	$[He]2s^2 2p^5$	^2P	0.00	0.00	0.00	0.00	0.00	0.00	−74.78974593
9	F^-	$[He]2s^2 2p^6$	^1S	0.00	0.00	0.00	0.00	0.00	0.00	−99.45945391
11	Na^-	$[Ne]3s^2$	^1S	0.7	0.7	0.0	0.0	0.0	0.0	−161.8551260
13	Al^-	$[Ne]3s^2 3p^2$	^3P	0.1	0.1	0.0	0.0	0.0	0.0	−241.8782653
14	Si^-	$[Ne]3s^2 3p^3$	^4S	0.0	0.0	0.0	0.0	0.0	0.0	−288.8896602
15	P^-	$[Ne]3s^2 3p^4$	^3P	0.0	0.0	0.0	0.0	0.0	0.0	−340.6988736
16	S^-	$[Ne]3s^2 3p^5$	^2P	0.0	0.0	0.0	0.0	0.0	0.0	−397.5384302
17	Cl^-	$[Ne]3s^2 3p^6$	^1S	0.0	0.0	0.0	0.0	0.0	0.0	−459.5769253
19	K^-	$[Ar]4s^2$	^1S	3.1	3.1	0.2	0.2	0.0	0.0	−599.1619170
21	Sc^-	$[Ar]4s^2 3d^2$	^3F	0.3	0.2	0.0	0.0	0.0	0.0	−759.6887738
22	Ti^-	$[Ar]4s^2 3d^3$	^4F	0.3	0.3	0.0	0.0	0.0	0.0	−848.3725498
23	V^-	$[Ar]4s^2 3d^4$	^5D	0.2	0.2	0.0	0.0	0.0	0.0	−942.8631322
24	Cr^-	$[Ar]4s^2 3d^5$	^6S	0	0	0	0	0	0	−1043.337097
25	Mn^-	$[Ar]4s^2 3d^6$	^5D	0	0	0	0	0	0	−1149.729110
26	Fe^-	$[Ar]4s^2 3d^7$	^4F	0	0	0	0	0	0	−1262.367074
27	Co^-	$[Ar]4s^2 3d^8$	^3F	1	1	1	0	1	0	−1381.351810
28	Ni^-	$[Ar]4s^2 3d^9$	^2D	0	0	0	0	0	0	−1506.821133
29	Cu^-	$[Ar]4s^2 3d^{10}$	^1S	0	0	0	0	0	0	−1638.964145
31	Ga^-	$[Ar]4s^2 3d^{10} 4p^2$	^3P	0	0	0	0	0	0	−1923.260381
32	Ge^-	$[Ar]4s^2 3d^{10} 4p^3$	^4S	0	0	0	0	0	0	−2075.394742
33	As^-	$[Ar]4s^2 3d^{10} 4p^4$	^3P	1	0	1	0	1	0	−2234.222940
34	Se^-	$[Ar]4s^2 3d^{10} 4p^5$	^2P	0	0	0	0	0	0	−2399.904726
35	Br^-	$[Ar]4s^2 3d^{10} 4p^6$	^1S	0	0	1	0	1	0	−2572.536273
37	Rb^-	$[Kr]5s^2$	^1S	5	5	1	0	0	0	−2938.354900
39	Y^-	$[Kr]5s^2 4d^1 5p^1$	^1D	18	18	3	3	1	1	−3331.683116
40	Zr^-	$[Kr]5s^2 4d^3$	^4F	1	1	1	0	1	0	−3538.994500
41	Nb^-	$[Kr]5s^2 4d^4$	^5D	0	0	0	0	0	0	−3753.578216
42	Mo^-	$[Kr]5s^2 4d^5$	^6S	0	0	0	0	0	0	−3975.526268
43	Tc^-	$[Kr]5s^2 4d^6$	^5D	0	0	0	−1	0	0	−4204.764631
44	Ru^-	$[Kr]5s^2 4d^7$	^4F	1	0	1	0	1	0	−4441.528477
45	Rh^-	$[Kr]5s^2 4d^8$	^3F	0	0	0	0	0	0	−4685.875582
46	Pd^-	$[Kr]5s^2 4d^9$	^2D	0	0	0	0	1	0	−4937.891544
47	Ag^-	$[Kr]5s^2 4d^{10}$	^1S	0	0	1	0	1	0	−5197.700050
49	In^-	$[Kr]5s^2 4d^{10} 5p^2$	^3P	0	0	1	0	1	0	−5740.175141
50	Sn^-	$[Kr]5s^2 4d^{10} 5p^3$	^4S	1	0	1	0	1	0	−6022.972657
51	Sb^-	$[Kr]5s^2 4d^{10} 5p^4$	^3P	1	0	1	0	1	0	−6313.481518
52	Te^-	$[Kr]5s^2 4d^{10} 5p^5$	^2P	1	0	2	0	2	0	−6611.827949
53	I^-	$[Kr]5s^2 4d^{10} 5p^6$	^1S	1	0	2	0	2	0	−6918.075883

B-spline set with $R = 60$, $\mathscr{B}^9_{40,60}$, yields HFR energies which are in excellent agreement with the NHF values for the anions. Although results have not been shown, $\mathscr{B}^9_{40,60}$ also gives HFR energies which are in perfect agreement with the ten-digit NHF values for the neutral atoms and cations.

4 Conclusion

In the present work, we studied the validity of the *B*-splines as a universal basis set for the HFR calculations of the neutral atoms He–Xe, cations Li^+–Xe^+, and anions H^-–I^-. We found that $\mathscr{B}^9_{40,40}$ and $\mathscr{B}^9_{40,60}$ give HFR energies which were excellent agreement with the ten-digit NHF results for the neutral atoms and cations and for the anions, respectively. Moreover, the HFR energies of the neutral atoms and cations calculated with $\mathscr{B}^9_{40,60}$ are also in excellent agreement with the ten-digit NHF results. Therefore, we conclude that $\mathscr{B}^9_{40,60}$ can be used as a universal basis set for the HFR calculations of the neutral atoms with $Z \leq 54$ and their singly charged ions.

We examined only the total energies of the atomic systems with *s*, *p*, or *d* orbitals. However, since examination of other properties, such as orbital energies, orbital cusps, or electron density at the nucleus, is also of interest, we will discuss these properties in the near future. Further, we will also study the applicability of the *B*-splines to *f* orbitals and to correlating orbitals with higher symmetries in post-Hartree–Fock calculations, such as the configuration interaction method or perturbation calculations. Work in this direction is in progress.

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