Theor Chim Acta (1995) 90: 27–39

Theoretica Chimica Acta

Relativistic Gaussian basis sets for radon through plutonium

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Summary. Relativistic Gaussian basis sets of neutral atoms Rn–Pu and ions Th^{+4},U^{+3} and Pu^{+3} in the configurations of average energies are presented. The exponent parameters of the basis sets are determined by least-squares fitting to the numerical Dirac–Fock wave functions. The total energies obtained are within 0.155 a.u. of the Dirac–Fock limits and the qualities of the basis sets are between double-zeta and triple-zeta in the valence parts. Using the exponent parameters the Breit interaction energies have been calculated by perturbation theory and the self-consistent field treatment.

Key words: Relativistic Gaussian basis sets – Radon – Actinides – Dirac–Coulomb Hamiltonian – Breit interaction

1. Introduction

We have hitherto reported relativistic Gaussian basis sets for atoms H [1, 2], He–Hg [3], and Tl–Rn [4]. We have calculated them for the configurations of average energies [5] using the Dirac–Coulomb Hamiltonian and adopted the scheme of kinetic energy balance [6] and the nucleus model of the uniformly charged sphere [7]. We have taken the exponent parameters (EP) for the relativistic basis sets from those of the nonrelativistically optimized basis sets [8, 9] without reoptimization and augmented some EPs for the relativistic calculations. We have optimized only the coefficients of the basis sets. The qualities of the calculated basis sets have turned out to be comparable to those of the numerical Dirac–Fock (NDF) wave functions [7]. The basis sets are expected to be adopted for reasonably accurate molecular calculations [10]. They were also used for the evaluation of Breit interaction (BI) energies of atoms He–Hg [11].

In the present paper we report relativistic Gaussian basis sets for neutral atoms Rn (atomic number $Z = 86$)–Pu ($Z = 94$) and ions Th^{+4}, U^{+3}, and Pu^{+3}. In this work we have adopted the least-squares method to determine the EPs of the basis sets and carried out least-squares fitting to the NDF wave functions [7, 12], since the nonrelativistically optimized high-quality basis sets are only available for Rn [9] and Th [13] and the optimization of the EPs are expensive even in nonrelativistic Hartree–Fock calculations. However, the qualities of the basis sets obtained

have turned out the same as those of previously reported basis sets [1–4] and can be compared favorably with those of the NDF wave functions [7, 12]. Using the calculated EPs we have also estimated the BI energies by first-order perturbation theory and the self-consistent field procedure. These basis sets are expected to be used for high-quality molecular calculations of actinide compounds.

In recent years Mohanty and Clementi [14] reported relativistic Gaussian basis sets for atoms He–Rn. Also, Da Silva et al. [15] gave relativistic Gaussian basis sets for some selected closed-shell atoms up to No. Some of their basis sets [14, 15] overlap with ours. However, the sizes of their basis sets are longer than ours so that they could be used for highly accurate calculations, especially for atoms.

2. Generation of the basis sets

For the generation of the basis sets we have employed almost the same computational procedures as those adopted previously [1–4]. However, in this work we have determined the EPs by least-squares fitting to the NDF wave functions computed using Desclaux's program [12]. Thus for each symmetry species the numerically generated wave functions of the large and the small component of the ith orbitals, $P(r)$ and $Q(r)$, were fitted by the corresponding Gaussian-type functions, $R^{\mathrm{L}}(\zeta; r)$ and $R^{\mathrm{S}}(\zeta; r)$, so that

$$I[\zeta, C] = \sum_i \left[w_i^{\mathrm{L}} \int_0^\infty \left[r^{-1} P_i(r) - \sum_{p=1}^{N} C_{ip}^{\mathrm{L}} R_p^{\mathrm{L}}(\zeta_p; r) \right]^2 \rho(r) r^2 \, \mathrm{d}r + w_i^{\mathrm{S}} \int_0^\infty \left[r^{-1} Q_i(r) - \sum_{p=1}^{N} C_{ip}^{\mathrm{S}} R_p^{\mathrm{S}}(\zeta_p; r) \right]^2 \rho(r) r^2 \, \mathrm{d}r \right] \tag{1}$$

has the minimum with respect to the variation of the EPs ζ and the expansion coefficients C. Here the large and the small component Gaussian-type functions are related by minimal kinetic balance [6]. The weight factors w^{L} and w^{S} should be chosen appropriately to take proper account of the role of the small components. After some trials (such that $w^{\mathrm{L}} = 1$ and $w^{\mathrm{S}} = c^2$, where c is the speed of light) we found it appropriate to choose that

$$(w_i^{\mathrm{L}})^{-1} = \int_0^\infty [r^{-1} P_i(r)]^2 r^2 \, \mathrm{d}r$$

$$(w_i^{\mathrm{S}})^{-1} = \int_0^\infty [r^{-1} Q_i(r)]^2 r^2 \, \mathrm{d}r \tag{2}$$

The weight function $\rho(r)$ was chosen to be $1/r$ so that the wave functions near the nuclei could be better fitted.

We have employed the program STEPIT [16] for the optimization of the EPs. The integrals needed in Eqs. (1) and (2) were obtained either analytically or using Simpson integration. In the region between the nuclei and the first integration points the NDF wave functions [12] are expressed in terms of power series. Hence we naturally tried to perform the integrations for this region analytically. However, the analytically performed integrations were sometimes not stable, giving unexpectedly large contributions in this region due to the largely cancelling (plus and

minus) coefficients of the power series of the numerical wave functions. Hence to estimate the contributions we instead adopted the numerical integration in this region, too. We have adopted the uniformly charged sphere model of atomic nuclei whose radii were calculated as $2.2677 \times 10^{-5} A^{1/3}$ (in a.u.) [7], where A is the atomic mass number. We have taken the speed of light as 137.037 a.u.

We found that the largest EPs of s-type basis functions could not be determined by least squares, since the positions of the maxima of the basis functions were calculated to be less than the first integration points of the NDF wave functions so that the numerical instabilities occurred sometimes. Hence we determined their optimum values by interpolation of total energies of three EPs around an EP estimated for each basis function. This procedure worked better than the least squares.

We began exploratory calculations on Rn using Faegri's nonrelativistic EP set of $(22s17p13d8f)$ [9] and tried to find the appropriate basis sizes which reproduced the NDF total energies within 0.1–0.2 a.u. and gave reasonable orbital energies. We found the least-squares fitted EP set of the size $(21s19p13d8f)$ appropriate; For the relativistic basis set we had to add two more p-type functions to represent especially the lowest $p_{1/2}$ orbital. However, we could delete one s-type function. This is due to our adoption of the uniformly charged sphere model of the atomic nucleus as compared to the point-charge model employed in the nonrelativistic calculation [9]. When we added one more s-type function and used 22 s-type Gaussians, we observed variational collapse [17]. Then using the EP set obtained for Rn, we found that for the next element Fr the appropriate basis size is $(24s19p13d8f)$; Here we have added three more s-type Gaussians since the $7s$ orbital is now occupied. Processing in this way we generated the relativistic basis sets for Rn–Pu.

In the actinide elements, particularly interesting atoms are Th, U, and Pu and in many cases they appear in ionic states. Thus we have also generated basis sets for ions Th^{+4}, U^{+3}, and Pu^{+3}.

Table 1 lists the obtained total energies. They are within 0.060 a.u. (Th^{+4}) to 0.155 a.u. (Rn) of the total energies of the NDF limits [7, 12]. The EPs of the relativistic basis sets are collected in Tables 2a–2f. As an example, the EPs of U are shown in semi-log plots in Fig. 1. They are not even-tempered [18] but can be represented better by the well-tempered scheme [19]. Also, in Table 3 examples of orbital energies for Th and U are compared with the NDF orbital energies. The qualities of the basis sets are between double-zeta and triple-zeta in the valence parts, judging from the expansion coefficients of the basis sets.

3. Breit interaction energies

In order to test further the qualities of the basis sets obtained and on their own merits, we have calculated the BI energies by first-order perturbation theory and by the self-consistent field treatment. The details of the calculational method are given in Ref. [11]. The BI energies obtained are shown in Table 4 where the PT results using the NDF wave functions are also compared.

From the table we see that the BI energies are about 0.1% of the total energies and the BI energies obtained by the SCF treatment are slightly smaller than those by the PT. These facts were also observed in the BI energies of He–Hg [11].

Table 1. Atomic total average energies. All values in a.u.

Atomic number	Atom	Conf.	Mass number	Basis size	$-E$(DFR)[a]	$-E$(NDF)[b]	ΔE[c]
86	Rn	$6p^6$	222	21, 19, 13, 8	23601.81752	23601.97256	0.15504
87	Fr	$7s^1$	223	24, 19, 13, 8	24307.93411	24308.04689	0.11278
88	Ra	$7s^2$	226	24, 19, 13, 8	25027.90997	25028.01715	0.10718
89	Ac	$6d^17s^2$	227	24, 19, 16, 8	25762.06579	25762.17598	0.11019
90	Th	$6d^27s^2$	232	24, 19, 16, 8	26510.56338	26510.67664	0.11326
	Th^{+4}	$6s^26p^2$	232	21, 19, 13, 8	26508.40092	26508.46117	0.06025
91	Pa	$5f^26d^17s^2$	231	24, 19, 16, 11	27274.00018	27274.12695	0.12677
92	U	$5f^36d^17s^2$	238	24, 19, 16, 11	28052.40137	28052.53288	0.13151
	U^{+3}	$5f^3$	238	21, 19, 13, 11	28051.23230	28051.30704	0.07474
93	Np	$5f^46d^17s^2$	237	24, 19, 16, 11	28846.53403	28846.67163	0.13760
94	Pu	$5f^67s^2$	244	24, 19, 13, 11	29656.07028	29656.21301	0.14273
	Pu^{+3}	$5f^5$	244	21, 19, 13, 11	29654.89123	29654.97146	0.08023

[a] Dirac–Fock–Roothaan calculation (present work)
[b] Numerical Dirac–Fock energy
[c] E(DFR)–E(NDF)

Table 2a. Exponent parameters of relativistic Gaussian basis sets

	s	*p*	*d*	*f*
Rn				
1	49828310	26787620	17119.15	725.3973
2	11829980	4371177	4001.603	227.7080
3	2869483	689876.1	1319.045	91.53638
4	783242.5	141348.7	514.9216	40.90340
5	232450.4	35199.47	221.7480	19.34950
6	73606.61	10219.03	101.4811	9.276750
7	24569.63	3353.757	48.18326	4.374237
8	8573.145	1216.855	22.75495	1.906473
9	3118.596	478.4033	10.81240	
10	1192.707	202.3651	5.139761	
11	402.2742	84.27031	2.346367	
12	176.8402	39.43159	1.031697	
13	68.46686	16.34476	0.4059063	
14	36.37844	7.919167		
15	14.23028	3.040547		
16	7.810254	1.418477		
17	2.531524	0.4950321		
18	1.459095	0.2030144		
19	0.5108893	0.07560041		
20	0.2699513			
21	0.1136493			
Fr				
1	49906670	26556750	13997.24	725.5254
2	12512270	4810708	3266.687	227.7823
3	3191242	780870.1	1079.423	91.86187
4	913466.9	162165.2	423.0567	41.25450
5	283901.9	40488.48	183.7445	19.60758
6	94316.52	11703.55	84.92793	9.462984
7	33174.53	3810.734	41.13057	4.502840
8	12281.82	1369.188	19.99305	1.991454
9	4764.808	532.6415	9.733785	
10	1931.999	222.4981	4.699889	
11	831.5736	92.20897	2.251164	
12	341.3424	42.78956	1.030649	
13	156.2268	17.91453	0.4264623	
14	60.36804	8.663856		
15	33.15781	3.396599		
16	13.08783	1.617752		
17	7.403852	0.5936700		
18	2.531853	0.2568611		
19	1.383749	0.09867149		
20	0.4183058			
21	0.1810748			
22	0.03032450			
23	0.01422464			
24	0.007468053			

Table 2b. Exponent parameters of relativistic Gaussian basis sets

	s	*p*	*d*	*f*
Ra				
1	49459510	27881180	14922.90	783.8458
2	12214480	4761031	3467.287	245.3169
3	3105817	768431.6	1142.386	98.60846
4	881224.1	158967.7	447.2824	44.18189
5	271704.8	39591.00	194.3614	21.00557
6	90014.79	11441.83	90.02458	10.15758
7	31730.32	3739.414	43.72305	4.851784
8	11797.49	1353.558	21.36595	2.159877
9	4600.707	531.5791	10.46318	
10	1876.675	224.2602	5.106062	
11	809.5721	94.19040	2.469890	
12	341.4412	43.97820	1.147122	
13	157.4480	18.73001	0.4871209	
14	61.66511	9.092748		
15	33.62230	3.664731		
16	13.65009	1.768150		
17	7.630201	0.6742512		
18	2.769412	0.3017844		
19	1.510736	0.1170584		
20	0.4930877			
21	0.2332460			
22	0.05486988			
23	0.03018168			
24	0.01544742			
1	51302340	29428390	14187.76	822.1441
2	12288470	4780940	33067.58	258.7940
3	3155113	772303.9	1090.243	104.5635
4	905668.2	159692.3	425.8263	46.99356
5	281131.3	39744.38	184.1772	22.39099
6	93277.91	11486.32	84.69180	10.85259
7	32850.65	3758.403	40.85140	5.203614
8	12217.18	1364.202	19.80815	2.332798
9	4772.672	537.9759	9.657749	
10	1950.676	228.0823	4.604305	
11	843.3556	96.47924	2.233463	
12	355.2562	45.24114	1.047442	
13	163.6841	19.43157	0.4450787	
14	64.76601	9.482648	0.1888619	
15	35.24579	3.880109	0.07775301	
16	14.43550	1.893247	0.03098107	
17	8.070128	0.732932		
18	2.961476	0.3383151		
19	1.643484	0.1320568		
20	0.5521987			
21	0.2710222			
22	0.07355447			
23	0.03930466			
24	0.01891598			

Table 2c. Exponent parameters of relativistic Gaussian basis sets

	s	*p*	*d*	*f*
Th				
1	52189530	30299830	15774.25	879.1677
2	12177270	5170216	3649.507	275.4211
3	3143123	857139.8	1198.903	110.7388
4	908425.7	179377.9	468.0927	49.61432
5	283933.0	44854.22	202.8519	23.62707
6	94711.69	12953.36	93.68744	11.46926
7	33421.81	4217.588	45.39704	5.519456
8	12418.04	1518.715	22.11228	2.492699
9	4845.068	593.2157	10.82814	
10	1979.859	248.7306	5.248522	
11	854.7774	104.6817	2.566468	
12	364.2565	48.73440	1.220732	
13	168.1652	21.07784	0.5337902	
14	67.25312	10.25904	0.2331874	
15	36.50258	4.263146	0.09766805	
16	15.09962	2.098983	0.03912315	
17	8.454397	0.8418696		
18	3.125715	0.3892551		
19	1.760772	0.1516746		
20	0.6075991			
21	0.3035794			
22	0.08489335			
23	0.04340613			
24	0.02077201			
Th				
1	48052450	34045120	18064.71	861.7169
2	12268740	6543040	4154.785	270.7326
3	3201807	1171291	1360.136	109.2848
4	932413.5	254930.0	530.7296	49.15076
5	292821.0	65264.94	230.1611	23.47579
6	98149.68	19092.45	106.7245	11.42286
7	34862.67	6257.776	51.91408	5.506099
8	13027.24	2260.321	25.56154	2.488499
9	5092.317	886.1345	12.63210	
10	2076.517	371.7309	6.282883	
11	894.4197	166.0357	3.054454	
12	372.1662	74.96945	1.446446	
13	170.5170	36.55193	0.6373909	
14	66.99645	16.14310		
15	36.47693	8.027414		
16	14.79580	3.318606		
17	8.332838	1.586227		
18	3.012172	0.5838767		
19	1.668777	0.2545392		
20	0.5669547			
21	0.2766164			

Table 2d. Exponent parameters of relativistic Gaussian basis sets

	s	*p*	*d*	*f*
Pa				
1	52477620	28558650	16078.34	683.3451
2	12260410	5271487	3708.018	212.6877
3	3166830	876262.4	1214.083	84.18280
4	914580.6	183540.2	472.6139	36.91260
5	285468.9	45846.29	204.3198	16.81001
6	95157.42	13213.34	94.12571	7.769601
7	33617.60	4297.659	45.47050	1.562305
8	12502.91	1548.131	22.02118	3.515675
9	4871.450	605.3411	10.74496	0.6704247
10	1986.490	254.1605	5.146168	0.2703264
11	855.3969	107.0991	2.508086	0.09661780
12	367.5243	49.92496	1.179600	
13	170.6363	21.56948	0.5008909	
14	68.01823	10.53433	0.2114116	
15	37.04489	4.376203	0.08634697	
16	15.21053	2.153610	0.03401952	
17	8.628358	0.8513270		
18	3.215399	0.3863850		
19	1.795169	0.1498807		
20	0.6240437			
21	0.3017299			
22	0.08083771			
23	0.04307496			
24	0.02045765			
Np				
1	48165900	32189820	16176.97	715.6914
2	12204240	5913894	3723.773	223.3371
3	3190238	1012679	1219.480	88.73400
4	937058.9	214485.6	474.8391	39.19934
5	296567.1	53711.96	205.4297	18.06309
6	99826.91	15421.38	94.75836	8.496088
7	35522.28	4973.800	45.84871	3.946944
8	13298.53	1772.275	22.27435	1.799588
9	5225.524	685.2761	10.94075	0.7927786
10	2143.086	284.3610	5.239059	0.3293536
11	926.6768	119.4569	2.559936	0.1219740
12	397.6837	55.22533	1.205769	
13	184.1411	24.02435	0.5132541	
14	74.07511	11.69109	0.2152000	
15	40.23531	4.915218	0.08754252	
16	16.55287	2.424536	0.03439865	
17	9.440492	0.9618143		
18	3.550529	0.4313330		
19	1.992028	0.1657181		
20	0.6909069			
21	0.3304962			
22	0.08274910			
23	0.04347100			
24	0.02093741			

Table 2e. Exponent parameters of relativistic Gaussian basis sets

	s	*p*	*d*	*f*
U				
1	48171220	30062560	16079.47	703.2615
2	12113820	5589055	3707.242	219.0811
3	3147013	948314.4	1215.799	86.84438
4	912190.1	200185.0	474.0402	38.22365
5	285123.9	50135.61	205.1856	17.51736
6	95179.62	14437.84	94.63173	8.173417
7	33651.45	4676.745	45.78370	3.752665
8	12511.46	1673.810	22.23856	1.692354
9	4869.811	649.7508	10.89752	0.7374815
10	1981.838	270.7284	5.229659	0.3025422
11	849.5540	113.7117	2.556736	0.1103255
12	370.1375	52.73747	1.205077	
13	172.9851	22.85757	0.5121164	
14	69.22380	11.13758	0.2154203	
15	37.71001	4.649110	0.08774074	
16	15.37485	2.291376	0.03447413	
17	8.819909	0.9059122		
18	3.336037	0.4089979		
19	1.857722	0.1579066		
20	0.6523634			
21	0.3124319			
22	0.08254175			
23	0.04313320			
24	0.02058815			
U^{+3}				
1	49681820	31967380	16708.05	782.0875
2	12161810	7110345	3842.526	243.7053
3	3186681	1299282	1261.764	97.18347
4	929989.5	284880.3	494.4259	43.17729
5	292501.2	72983.23	215.8886	20.17854
6	98075.42	21266.15	100.8138	9.618463
7	34774.49	6919.401	49.46395	2.120388
8	13007.95	2475.489	24.55634	4.557873
9	5116.100	960.0750	12.25171	0.9605607
10	2100.568	398.3426	6.119784	0.4195179
11	909.6898	176.2717	3.037391	0.1769041
12	386.3560	78.86171	1.448102	
13	178.4142	38.25612	0.6309062	
14	71.87812	16.75178		
15	38.82372	8.341891		
16	15.96080	3.461300		
17	9.004208	1.635670		
18	3.273826	0.5949836		
19	1.801699	0.2445162		
20	0.6113463			
21	0.2818689			

Table 2f. Exponent parameters of relativistic Gaussian basis sets

	s	*p*	*d*	*f*
Pu				
1	48464610	32888730	20092.79	711.4214
2	12145980	5963289	4571.980	221.4818
3	3244937	1028455	1487.586	87.67007
4	971117.0	218442.0	578.4454	38.56573
5	313594.2	54745.67	250.4641	17.64591
6	107666.6	15718.07	116.0525	8.239404
7	38992.04	5065.534	56.48332	3.789557
8	14812.50	1802.534	27.82415	1.698378
9	5869.173	695.8576	13.79914	0.7268729
10	2411.162	288.6399	6.880177	0.2898843
11	1039.002	120.8096	3.383976	0.1022410
12	430.9253	55.97065	1.589818	
13	196.7729	24.12005	0.6694715	
14	77.23350	11.83213		
15	42.31483	4.929549		
16	16.83708	2.432499		
17	9.828811	0.9449382		
18	3.623228	0.4160854		
19	2.031006	0.1591531		
20	0.6982056			
21	0.3212178			
22	0.06655861			
23	0.03272889			
24	0.01651512			
Pu^{+3}				
1	48445930	33718550	19897.04	908.0124
2	12118080	7780318	4533.219	283.0639
3	3225266	1443920	1476.931	113.1123
4	957700.4	318255.1	575.0067	50.30629
5	305595.8	81507.83	249.3644	23.59672
6	103622.9	23650.46	115.7817	11.29222
7	37143.55	7645.656	56.48291	5.389511
8	13992.38	2715.620	27.90768	2.528671
9	5508.298	1045.947	13.88818	1.150259
10	2257.824	431.2670	6.956196	0.5008732
11	975.0130	189.9977	3.443365	0.2083699
12	413.8124	84.54502	1.635029	
13	190.9095	40.94382	0.7060229	
14	75.84074	17.87787		
15	41.33016	8.945764		
16	16.61012	3.750004		
17	9.595160	1.769018		
18	3.537000	0.6449760		
19	1.942424	0.2619453		
20	0.6663531			
21	0.3040836			

Table 3. Orbital energies (in a.u.) for Th and U

	Th		U	
Orbital	$-\varepsilon$ (DFR)[a]	$-\varepsilon$ (NDF)[b]	$-\varepsilon$ (DFR)[a]	$-\varepsilon$ (NDF)[b]
$1s$	4058.5144	4058.510	4279.2388	4279.233
$2s$	758.56681	758.5649	806.16201	806.1592
$2p_{1/2}$	729.87993	729.8974	776.35412	776.3734
$2p_{3/2}$	603.58577	603.5883	635.56828	635.5705
$3s$	193.11474	193.1139	206.61134	206.6098
$3p_{1/2}$	180.13122	180.1369	193.09366	193.0996
$3p_{3/2}$	150.89388	150.8956	160.32096	160.3225
$3d_{3/2}$	130.31089	130.3103	139.01941	139.0184
$3d_{5/2}$	124.35885	124.3580	132.42020	132.4188
$4s$	50.194861	50.19464	54.324671	54.32415
$4p_{1/2}$	44.347075	44.34922	48.191941	48.19418
$4p_{3/2}$	36.714910	36.71603	39.540079	39.54128
$4d_{3/2}$	27.324823	27.32470	29.733976	29.73370
$4d_{5/2}$	25.902194	25.90193	28.130974	28.13057
$4f_{5/2}$	13.535187	13.53488	15.204544	15.20451
$4f_{1/2}$	13.177113	13.17677	14.792451	14.79231
$5s$	11.568164	11.56819	12.596284	12.59631
$5p_{1/2}$	9.2494724	9.250241	10.126989	10.12791
$5p_{3/2}$	7.5061066	7.506728	8.0919905	8.092764
$5d_{3/2}$	3.9814107	3.981507	4.3512258	4.351381
$5d_{5/2}$	3.7185948	3.718662	4.0415329	4.041650
$5f_{5/2}$	–	–	0.34672416	0.3470423
$5f_{7/2}$	–	–	0.31928677	0.3195910
$6s$	2.0658116	2.066002	2.1376802	2.137963
$6p_{1/2}$	1.3172293	1.317635	1.3425673	1.343107
$6p_{3/2}$	1.0016567	1.001021	0.98419600	0.9846814
$6d_{3/2}$	0.22274669	0.2229780	0.19239388	0.1927551
$6d_{5/2}$	0.21044487	0.2106937	0.18288813	0.1832755
$7s$	0.20932969	0.2094491	0.20220699	0.2023518

[a] Present calculation
[b] Numerical Dirac–Fock energy

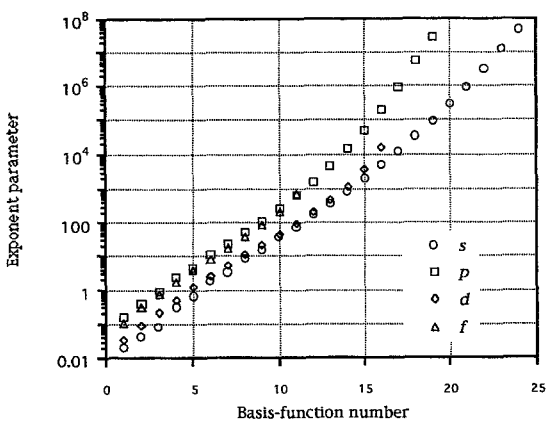

Fig. 1. Exponent parameters of U

Table 4. Breit interaction energies E_B (in a.u.)

Atom	E_B(NDF-PT)[a]	E_B(DFR-PT)[b]	E_B(DFR-SCF)[c]	ΔE_B[d]
Rn	29.3092	29.39568	29.35098	0.04469
Fr	30.5656	30.65478	30.60762	0.04716
Ra	32.0182	31.95576	31.90603	0.04973
Ac	33.2051	33.29970	33.24728	0.05242
Th	34.5902	34.68761	34.63238	0.05523
Pa	36.0143	36.11435	36.05618	0.05817
U	37.4869	37.58963	37.52840	0.06123
Np	39.0085	39.11384	39.04941	0.06443
Pu	40.5748	40.68276	40.61501	0.06776

[a] Computed by perturbation theory using numerical Dirac–Fock wave functions
[b] Computed by perturbation theory (present work)
[c] Computed by SCF procedure (present work)
[d] E_B(DFR-PT)–E_B(DFR-SCF) (computed using the present basis sets)

4. Discussion and conclusions

In the present paper we have reported relativistic Gaussian basis sets for atoms Rn–Pu and ions Th^{+4}, U^{+3}, and Pu^{+3}. For the computation of the basis sets we have adopted almost the same methods as those employed previously for atoms H–Hg [14]. However, in the present work, we have adopted the least-squares method to determine the EPs and found that this method worked very well, yielding total energies within 0.1–0.2 a.u. of the NDF wave functions. The qualities of the basis sets are between the double-zeta and the triple-zeta. Hence we expect that these basis sets could be employed for high-quality molecular calculations. We have also estimated the BI energies. The results show the same tendency as the one observed in the previous calculations of atoms He–Hg [11].

More details of the basis sets reported in the present paper may be obtained from the second author upon request.

References

1. Matsuoka O, Okamura K (1989) Bull Univ Electro-Comm 2:13
2. Yamamoto H, Matsuoka O (1992) Bull Univ Electro-Comm 5:23
3. Okada S, Matsuoka O (1989) J Chem Phys 91:4193
4. Matsuoka O, Okada S (1989) Chem Phys Lett 155:547
5. Desclaux JP, Moser CM, Verhaegen V (1971) J Phys B 4:296
6. Stanton RE, Havriliak S (1984) J Chem Phys 81:1910
7. Desclaux JP (1973) At Data Nucl Tables 12:311
8. Huzinaga S, Klobukowski M (1986) J Mol Struct (Theochem) 135:403
9. Faegri Jr K (1987) Theo Chim Acta 72:297
10. Matsuoka O, Pisani L, Clementi E (1993) Chem Phys Lett 202:13
11. Okada S, Shinada M, Matsuoka O (1990) J Chem Phys 93:5013
12. Desclaux JP (1975) Comp Phys Comm 9:31; (1977) Comp Phys Comm 13:71
13. Marian CM, Wahlgren U, Gropen O, Pyykko P (1988) J Mol Struct (Theochem) 169:339
14. Mohanty A, Clementi E (1990) J Chem Phys 93:1829

15. Da Silva ABF, Malli GL, Ishikawa Y (1993) Phys Rev A47:143; (1993) Can J Chem 71:1713
16. Chandler JP (1969) Quantum chemistry program exchange. Indiana University, Bloominton Indiana
17. Kutzelnigg W (1984) Int J Quantum Chem 25:107
18. Ruedenberg K, Raffenetti RC, Bardo RD (1973) In: Smith DW (ed), Proc 1972 Boulder Conf Theoretical Chem, vol 164. Wiley, New York
19. Huzinaga S, Klobukowski M, Tatewaki H (1985) Can J Chem 63:1812