PHYSICAL REVIEW A VOLUME 51, NUMBER 1 JANUARY 1995

6*s* and 4*f* ionized states of the lanthanides calculated by numerical and analytical Hartree-Fock methods

Hiroshi Tatewaki
Computation Center, Nagoya City University, Nagoya, Aichi 467, Japan

Masahiro Sekiya and Fukashi Sasaki
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060, Japan

Osamu Matsuoka
Department of Physics, The University of Electro-Communications, Chofu, Tokyo 182, Japan

Toshikatsu Koga
Department of Applied Chemistry, Muroran Institute of Technology, Muroran, Hokkaido 050, Japan

(Received 26 July 1994)

The ground states, as well as the 6*s* and 4*f* ionized states of Ba, Cs, and lanthanide atoms from La to Lu, are calculated with the nonrelativistic numerical Hartree-Fock (HF) method and an analytical HF method with Gaussian-type functions (GTF's). It is shown that the nonrelativistic HF calculations well reproduce the experimental trends on the 6*s* and 4*f* electron ionizations, although the calculated 6*s* ionization potentials (IP's) are smaller and the calculated 4*f* IP's are larger than those given by experiment. The relativistic HF calculations with GTF's are also performed on some selected atoms. The 6*s* IP's given by the relativistic HF method are closer to experiment than those given by the nonrelativistic HF methods. The relativistic corrections make 4*f* IP's smaller than those of experiment. Since the correlation effects increase the IP's obtained by the HF calculations, the inclusion of the relativistic effects is indispensable in discussing IP's quantitatively.

PACS number(s): 31.15.−p, 31.30.Jv

Recently lanthanide chemistry and physics have experienced tremendous growth, for example, in the field of catalysts [1] and high temperature superconductors [2]. It would be highly desirable to elucidate the electronic structure of lanthanide atoms at least in the Hartree-Fock (HF) approximation. For these atoms, relativistic [3,4] and nonrelativistic [5–8] numerical Hartree-Fock (NHF) calculations were performed mainly on the ground states. Fraga and coworkers [7] gave the first, second, and third ionization potentials (IP's) for the atoms but their results have been found to be insufficiently accurate [9].

In this paper we discuss (1) the accurate nonrelativistic HF energies for lanthanide atoms and their positive ions, (2) the characteristics of the 4*f* levels, (3) the quality of the published large Gaussian-type-function (GTF) basis set for the ground states when applied to the ionized states, and (4) the influences of the relativistic effects. For this purpose, we first performed NHF computations for the ground states as well as the 6*s* and 4*f* electron ionized states. Present NHF total energies are accurate to nine significant figures as the previous calculations for the excited states of lighter atoms ($Z \leq 36$) [10] and those for the positively and negatively charged ions ($Z \leq 54$) [9]. We next calculated the analytical restricted Hartree-Fock (RHF) energies for the ground and ionized states, using well-tempered Gaussian-type functions [11,12] in order to see the accuracy of the most flexible GTF basis sets that are available in the molecular calculations. Finally, relativistic HF calculations were performed.

The atoms calculated are Cs, Ba, and lanthanides La through Lu. The electronic configurations adapted for the ground states are those of experiments [13,14];

Cs	$(6s)^1(5p)^6$
Ba	$(6s)^2(5p)^6$
La	$(6s)^2(5p)^6(5d)^1$
Ce	$(6s)^2(5p)^6(5d)^1(4f)^1$
Pr–Eu and Tb–Yb	$(6s)^2(5p)^6(5d)^0(4f)^m$ ($m=3$–7 and 9–14)
Gd	$(6s)^2(5p)^6(5d)^1(4f)^7$
Lu	$(6s)^2(5p)^6(5d)^1(4f)^{14}$.

1050-2947/95/51(1)/197(7)/$06.00

TABLE I. Total energies, ionization potentials, and excitation energies of the ions relative to the ground state of the neutral atoms calculated by RHF and NHF methods. Δ gives the difference between RHF and NHF.

							Total energies			IP's and excitation energies of ions		
Z	State		6s	5p	5d	4f	RHF[a] (a.u.)	NHF (a.u.)	Δ (a.u.)	RHF (eV)	NHF (eV)	Expt.[b] (eV)
55	Cs$^+$	^3P	1	5	0	0	−7 553.300 85	−7 553.301 09	0.000 25	17.212	17.212	
55	Cs$^+$	^1S	0	6	0	0	−7 553.810 08	−7553.810 32	0.000 25	3.356	3.356	3.893
55	Cs	^2S	1	6	0	0	−7 553.933 41	−7 553.933 65	0.000 25	0.000	0.000	0.000
56	Ba$^+$	^2P	2	5	0	0	−7 882.699 53	−7 882.699 70	0.000 17	22.969	22.969	
56	Ba$^+$	^2S	1	6	0	0	−7 883.391 71	−7 883.391 88	0.000 17	4.134	4.134	5.210
56	Ba	^1S	2	6	0	0	−7 883.543 65	−7 883.543 82	0.000 17	0.000	0.000	0.000
57	La$^+$	^3F	2	5	1	0	−8 220.121 19	−8 220.121 36	0.000 17	25.723	25.723	
57	La$^+$	^3G	2	5	0	1	−8 220.213 33	−8 220.213 50	0.000 17	23.216	23.216	
57	La$^+$	^3H	0	6	0	2	−8 220.748 76	−8 220.748 94	0.000 18	8.647	8.646	9.973
57	La$^+$	^1S	2	6	0	0	−8 220.831 39	−8 220.831 56	0.000 17	6.398	6.398	6.494
57	La$^+$	^3D	1	6	1	0	−8 220.908 44	−8 220.908 61	0.000 17	4.302	4.302	5.812
57	La$^+$	^3F	1	6	0	1	−8 220.910 03	−8 220.910 20	0.000 17	4.258	4.258	5.577
57	La	^2F[c]	2	6	0	1	−8 221.063 63	−8 221.063 81	0.000 17	0.079	0.079	(≤ 1.87)
57	La	^2D	2	6	1	0	−8 221.066 53	−8 221.066 70	0.000 17	0.000	0.000	0.000
58	Ce$^+$	^4I	2	5	0	2	−8 566.052 99	−8 566.053 16	0.000 18	22.300	22.300	
58	Ce$^+$	^2D	2	6	1	0	−8 566.330 73	−8 566.330 91	0.000 18	14.742	14.742	(11.5)
58	Ce$^+$	^2G	1	6	1	1	d	−8 566.707 64			4.491	7.838
58	Ce$^+$	^2F	2	6	0	1	−8 566.612 19	−8 566.612 37	0.000 18	7.083	7.083	6.678
58	Ce$^+$	^4H	1	6	0	2	−8 566.764 38	−8 566.764 55	0.000 18	2.942	2.942	5.944
58	Ce$^+$	^4H	0	6	2	1	−8 566.743 67	−8 566.743 86	0.000 19	3.505	3.505	5.466
58	Ce	^3H[c]	2	6	0	2	−8 566.919 40	−8 566.919 57	0.000 17	−1.276	−1.276	0.590
58	Ce	^1G	2	6	1	1	−8 566.872 50	−8 566.872 68	0.000 18	0.000	0.000	0.000
59	Pr$^+$	^5K	2	5	0	3	−8 920.291 79	−8 920.291 97	0.000 18	24.192	24.192	
59	Pr$^+$	^3H	2	6	0	2	−8 920.820 70	−8 920.820 88	0.000 18	9.800	9.800	(7.40)
59	Pr$^+$	^5I	1	6	0	3	−8 921.024 51	−8 921.024 70	0.000 18	4.254	4.254	5.422
59	Pr	^4I	2	6	0	3	−8921.180 84	−8 921.181 02	0.000 19	0.000	0.000	0.000
60	Nd$^+$	^6K	2	5	0	4	−9 282.968 76	−9 282.968 94	0.000 18	24.870	24.871	
60	Nd$^+$	^4I	2	6	0	3	−9 283.519 62	−9 283.519 80	0.000 18	9.881	9.881	(7.66)
60	Nd$^+$	^6I	1	6	0	4	−9 283.725 17	−9 283.725 36	0.000 19	4.288	4.288	5.489
60	Nd	^5I	2	6	0	4	−9 283.882 75	−9 283.882 94	0.000 19	0.000	0.000	0.000
61	Pm$^+$	^7I	2	5	0	5	−9 654.163 15	−9 654.163 34	0.000 19	25.459	25.459	
61	Pm$^+$	^5I	2	6	0	4	−9 654.736 05	−9 654.736 24	0.000 19	9.870	9.870	(7.66)
61	Pm$^+$	^7H	1	6	0	5	−9 654.939 98	−9 654.940 17	0.000 19	4.321	4.321	5.554
61	Pm	^6H	2	6	0	5	−9 655.098 77	−9 655.098 96	0.000 19	0.000	0.000	0.000
62	Sm$^+$	^8G	2	5	0	6	−10 034.004 9	−10 034.005 1	0.000 2	25.780	25.780	
62	Sm$^+$	^6H	2	6	0	5	−10 034.543 0	−10 034.543 2	0.000 2	11.139	11.139	(8.61)
62	Sm$^+$	^8F	1	6	0	6	−10 034.792 4	−10 034.792 6	0.000 2	4.352	4.352	5.631
62	Sm	^7F	2	6	0	6	−10 034.952 3	−10 034.952 5	0.000 2	0.000	0.000	0.000
63	Eu$^+$	^9P	2	5	0	7	−10 422.599 5	−10 422.599 7	0.000 2	25.669	25.669	
63	Eu$^+$	^7F	2	6	0	6	−10 423.068 5	−10 423.068 7	0.000 2	12.906	12.906	(9.76)
63	Eu$^+$	^9S	1	6	0	7	−10 423.381 8	−10 423.382 0	0.000 2	4.381	4.381	5.666
63	Eu	^8S	2	6	0	7	−10 423.542 8	−10 423.543 0	0.000 2	0.000	0.000	0.000
64	Gd$^+$	^{10}F	2	5	1	7	−10 819.618 0	−10 819.618 2	0.000 2	28.381	28.381	
64	Gd$^+$	^8G	2	5	0	8	−10 819.662 6	−10 819.662 8	0.000 2	27.168	27.168	
64	Gd$^+$	^8H	2	6	1	6	−10 819.892 4	−10 819.892 6	0.000 1	20.913	20.916	(17.1)
64	Gd$^+$	^8F	1	6	0	8	−10 820.453 8	−10 820.454 0	0.000 2	5.639	5.639	7.132
64	Gd$^+$	^8S	2	6	0	7	−10 820.413 1	−10 820.413 3	0.000 2	6.745	6.745	6.568
64	Gd$^+$	^{10}D	1	6	1	7	−10 820.494 7	−10 820.494 9	0.000 3	4.525	4.525	6.141
64	Gd	^7F[c]	2	6	0	8	−10 820.617 1	−10 820.617 3	0.000 2	1.194	1.194	1.357
64	Gd	^9D	2	6	1	7	−10 820.661 0	−10 820.66 12	0.000 4	0.000	0.000	0.000
65	Tb$^+$	^7I	2	5	0	9	−11 225.592 1	−11 225.592 3	0.000 2	26.560	26.560	
65	Tb$^+$	^7F	2	6	0	8	−11 226.291 2	−11 226.291 4	0.000 2	7.537	7.537	(6.53)
65	Tb$^+$	^7H	1	6	0	9	−11 226.402 6	−11 226.402 8	0.000 2	4.505	4.505	5.852
65	Tb	$^6\mathrm{H}$	2	6	0	9	−11 226.568 1	−11 226.568 4	0.000 2	0.000	0.000	0.000
66	Dy$^+$	^6K	2	5	0	10	−11 640.447 2	−11 640.447 6	0.000 4	27.344	27.345	
66	Dy$^+$	$^6\mathrm{H}$	2	6	0	9	−11 641.127 8	−11 641.128 3	0.000 4	8.823	8.825	7.456
66	Dy$^+$	^6I	1	6	0	10	−11 641.284 4	−11 641.284 9	0.000 5	4.564	4.564	5.927

TABLE I. (Continued)

						Total energies			IP's and excitation energies of ions		
Z	State	6s	5p	5d	4f	RHF[a] (a.u.)	NHF (a.u.)	Δ (a.u.)	RHF (eV)	NHF (eV)	Expt.[b] (eV)
66	Dy ^{5}I	2	6	0	10	−11 641.452 1	−11 641.452 6	0.000 5	0.000	0.000	0.000
67	Ho^{+} ^{5}K	2	5	0	11	−12 064.251 1	−12 064.251 6	0.000 5	28.249	28.251	
67	Ho^{+} ^{5}I	2	6	0	10	−12 064.977 5	−12 064.977 9	0.000 4	8.485	8.487	(7.26)
67	Ho^{+} ^{5}I	1	6	0	11	−12 065.119 5	−12 065.120 0	0.000 5	4.621	4.621	6.018
67	Ho ^{4}I	2	6	0	11	−12 065.289 3	−12 065.289 8	0.000 5	0.000	0.000	0.000
68	Er^{+} ^{4}I	2	5	0	12	−12 497.080 1	−12 497.080 5	0.000 5	29.174	29.176	
68	Er^{+} ^{4}I	2	6	0	11	−12 497.854 4	−12 497.854 9	0.000 5	8.103	8.105	(6.97)
68	Er^{+} ^{4}H	1	6	0	12	−12 497.980 3	−12 497.980 9	0.000 5	4.677	4.678	6.101
68	Er ^{3}H	2	6	0	12	−12 498.152 2	−12 498.152 8	0.000 6	0.000	0.000	0.000
69	Tm^{+} ^{3}G	2	5	0	13	−12 939.071 4	−12 939.071 9	0.000 5	29.997	30.000	
69	Tm^{+} ^{3}H	2	6	0	12	−12 939.831 4	−12 939.832 0	0.000 5	9.316	9.318	7.728
69	Tm^{+} ^{3}F	1	6	0	13	−12 939.999 9	−12 940.000 5	0.000 6	4.731	4.732	6.184
69	Tm ^{2}F	2	6	0	13	−12 940.173 8	−12 940.174 4	0.000 6	0.000	0.000	0.000
70	Yb^{+} ^{2}P	2	5	0	14	−13 390.330 9	−13 390.331 4	0.000 6	30.603	30.605	
70	Yb^{+} ^{2}F	2	6	0	13	−13 391.045 8	−13 391.046 3	0.000 5	11.151	11.153	8.910
70	Yb^{+} ^{2}S	1	6	0	14	−13 391.279 7	−13 391.280 3	0.000 6	4.784	4.785	6.254
70	Yb ^{1}S	2	6	0	14	−13 391.455 6	−13 391.456 2	0.000 6	0.000	0.000	0.000
71	Lu^{+} ^{3}F	2	5	1	14	−13 850.566 0	−13 850.567 5	0.001 5	33.750	33.754	
71	Lu^{+} ^{3}H	2	6	1	13	−13 851.091 6	−13 851.093 0	0.001 5	19.450	19.455	(16.2)
71	Lu^{+} ^{3}D	1	6	1	14	−13 851.623 3	−13 851.624 9	0.001 6	4.980	4.981	6.888
71	Lu^{+} ^{1}S	2	6	0	14	−13 851.599 5	−13 851.601 0	0.001 5	5.630	5.633	5.426
71	Lu ^{2}D	2	6	1	14	−13 851.806 4	−13 851.808 0	0.001 6	0.000	0.000	0.000

[a] The number of the primitive GTF's for the respective atoms is as follows: (30s,23p,17d) for Cs and Ba; (30s,23p,22d,14f) for La, Ce, and Gd except for La ^{3}H where (30s,23p,22d,17f) are employed; (30s,23p,17d,14f) for Pr through Eu and also Tb; (29s,22p,16d,13f) for Dy through Yb; and (28s,21p,20d,12f) for Lu. The well-tempered basis sets [12] were obtained through the anonymous ftp of kamuy.chem.ualberta.ca

[b] The first ionization potentials are those given in Ref. [13]. The excited states for neutral atoms and ions are given in Ref. [14,15], respectively. The number in the parentheses are estimated ones (see Ref. [15]).

[c] Excited states in the neutral atoms.

[d] The program used cannot handle this state.

The states arising from $(6s)^2(5p)^6(5d)^0(4f)^m$ are also investigated for La ($m=1$), Ce ($m=2$), and Gd ($m=8$), since sometimes theorists treated them as the ground states. The calculated ionized states are those being deprived of the 6s or 4f electrons. The ionized states with the highest spin are mainly considered but other ionized states are also taken into account for La, Ce, and Gd. When we calculated analytical RHF energies for the states with 5d electrons, we always augmented an extra five diffuse d GTF's to those of Huzinaga and Klobukowski [12] except for Lu, where two d GTF's were augmented, since the well-tempered GTF's are prepared for the states with $(6s)^2(5p)^6(5d)^0(4f)^m$. We also augmented three diffuse f GTF's for La ^{3}H, where the number of 4f electrons is increased by one compared with ^{2}F of Huzinaga and Klobukowski [12].

The total energies, the differences in the total energies between NHF and RHF (Δ), IP's, and the excitation energies of the ions relative to the ground state of the neutral atoms obtained by the present calculations and experiments [13–15] are collected in Table I. We see that the total energy differences between NHF and RHF are quite small, indicating that well-tempered GTF's generated by Huzinaga and Klobukowski [12] are very reliable even in the ionized states. In Ce the calculated ground state is $(6s)^2(5p)^6(5d)^0(4f)^2\,{}^3H$ whereas the experimental ground state is $(6s)^2(5p)^6(5d)^1(4f)^1\,{}^1G$. Brewer [14] pointed out that the configuration interaction calculations were necessary in order to get the proper ground state for this atom; it will, however, be shown that the inclusion of the relativistic effects is also indispensable.

For La through Eu, both the calculated (∼4.3–4.5 eV) and experimental (∼5.4–5.8 eV) 6s IP's are almost constant with a sole exception of the experimental value of Ce (7.8 eV). After Tb, the IP gradually increases. The NHF and RHF calculations give 5.0 eV for Lu, while the experimental value is 6.9 eV. The experimental 6s IP's are always larger than the HF values. The electron correlation effects, which will be discussed later, should be included for better agreement. We see later that the relativistic corrections increase the 6s IP's by 0.3–0.7 eV, which means to remedy 20–30 % of the error found in the nonrelativistic calculations.

Although the calculated 4f IP's are 1–3 eV greater than those of experiment, NHF and RHF calculations describe the experimental trend well, when we move across the lanthanide atoms. Here we note the sudden increase of IP at Gd; the $4f$ electron IP's by experiment are 9.8, 17.1, and 6.5 eV for Eu, Gd, and Tb, respectively. The anomaly at Gd found by experiment is well simulated in the nonrelativistic HF calculations. The ground configurations of Eu and other atoms are $6s^24f^m$, while that of Gd is $6s^24f^75d^1(^9D)$ instead of being $6s^24f^8(^7F)$. In $6s^24f^75d^1$, the $5d$ orbital is expected to be much broader ($\langle r \rangle_{5d}$ for $^9D=2.463$ a.u.) than the $4f$ orbital ($\langle r \rangle_{4f}$ for $^9D=0.789$ a.u.); therefore the screening effects on the f shell electrons caused by one $5d$ electron are expected to be smaller than those caused by one $4f$ electron. Moreover, the configuration $6s^24f^75d^1$ makes it possible that all the electrons in the f shell keep up spins. The $4f$ electrons in $6s^24f^75d^1\,{}^9D$ thus are contracted compared with that of ^7F ($\langle r \rangle_{4f}$ for $^9D=0.789$ a.u. but $\langle r \rangle_{4f}$ for $^7F=0.834$ a.u.), making absolute values of exchange integrals and nuclear attraction energies larger for the $4f$ electrons. The $4f$ electrons in ^9D become energetically very stable. (The $4f$ orbital energy is -28.39 eV for ^9D and it is -18.92 eV for ^7F. See also IP's of Gd in Table I.)

The IP's for $5p$ electrons are also collected in Table I. The IP's for these electrons are large compared with those of $4f$ electrons.

The mean value of r, orbital energies, and IP's for the $6s$ and $4f$ electrons are summarized in Table II. We see that the $6s$ orbitals are diffuse. The differences between the IP's given by ΔSCF and the $6s$ orbital energy are small, indicating that the Koopmans theorem works for the $6s$ ionization: here ΔSCF means the total energy difference between the neutral and ionized systems calculated with the self-consistent-field (SCF) method, namely, the HF method. On the other hand, we may see that the $4f$ orbitals are contracted and the differences between the IP's given by ΔSCF and the Koopmans theorem are quite large. The ionization of the electrons in the outermost $6s$ shell causes small reorganization on the whole electron distributions whereas the inner $4f$ electron ionization, namely, the appearance of the hole in the inner shell, causes larger reorganization effects. We cannot use the Koopmans theorem for the $4f$ electron ionization.

We note sudden decrease of $\langle r \rangle_{6s}$ and $\langle r \rangle_{4f}$ in Gd ^9D. The decrease of $\langle r \rangle_{6s}$ in ^9D arises from the electron being in the $5d$ orbital instead of being in the $4f$ orbital. These sudden decreases are consistent with the sudden increase of the $6s$ and $4f$ IP's of Gd shown in Table II.

We see that $5p$ IP's are considerably larger than $4f$ ones. Although we have not displayed in Table II the mean distances $\langle r \rangle$ for $5p$, they are large compared with those of $4f$. For example, $\langle r \rangle_{5p}$ for Nd is 1.786 a.u. whereas $\langle r \rangle_{4f}$ is 0.955 a.u. The energetic and spatial relations between $5s$ and $4f$ electrons are similar to those between $5p$ and $4f$. The $4f$ electrons which are energetically bound loosely are encircled with $5s$ and $5p$ electrons which are energetically bound tightly. The atomic HF calculations indicate that the $4f$ electrons are protected by $5s$ and $5p$ electrons from the outer perturbations. We may expect that the characteristics of the $4f$ electrons in the atoms hold in molecules, complexes, and solids.

We recall that the nonrelativistic HF calculations always gave larger $4f$ IP's than those of experiment, although they simulate the experimental trend quite well. Since the correlation effects increase as the number of electron pairs increases, the correlation effects are expected to be larger in the ground state than in the ionized states. One may thus see that inclusion of the correlation effects further enlarges the IP's. We will discuss whether the inclusion of the relativistic effect could reduce $4f$ IP's in the next paragraph.

Using the same numbers and exponents of GTF's [12] adapted for RHF, we have performed relativistic HF cal-

TABLE II. Mean distance of r, orbital energies, and ionization potentials for $6s$ and $4f$ electrons.

			$6s$				$4f$			
	State		$\langle r \rangle$ (a.u.)	$-\varepsilon$ (eV)	IP (NHF) (eV)	IP (expt.) (eV)	$\langle r \rangle$ (a.u.)	$-\varepsilon$ (eV)	IP (NHF) (eV)	IP (expt.)[a] (eV)
55	Cs	^2S	6.3059	3.366	3.356	3.893				
56	Ba	^1S	5.2658	4.286	4.134	5.210				
57	La	^2D	4.9312	4.637	4.302	5.812				
58	Ce	^1G	4.8885	4.664	4.491	7.838	1.0011	19.41	14.742	(11.5)
69	Pr	^4I	5.0524	4.460	4.254	5.422	0.9985	14.94	9.800	(7.40)
60	Nd	^5I	4.9958	4.512	4.288	5.489	0.9546	16.21	9.881	(7.66)
61	Pm	^6H	4.9418	4.560	4.321	5.554	0.9185	17.10	9.870	(7.66)
62	Sm	^7F	4.8914	4.607	4.352	5.631	0.8850	18.13	11.139	(8.61)
63	Eu	^8S	4.8443	4.653	4.381	5.666	0.8536	19.37	12.906	(9.76)
64	Gd	^9D	4.5797	4.990	4.525	6.141	0.7890	28.39	20.916	(17.1)
65	Tb	^6H	4.7466	4.748	4.505	5.852	0.8126	18.92	7.537	(6.53)
66	Dy	^5I	4.7020	4.792	4.564	5.927	0.7918	19.13	8.825	7.456
67	Ho	^4I	4.6589	4.838	4.621	6.018	0.7724	19.28	8.487	(7.26)
68	Er	^3H	4.6172	4.882	4.678	6.101	0.7542	19.37	8.105	(6.97)
69	Tm	^2F	4.5773	4.925	4.732	6.184	0.7366	19.57	9.318	7.728
70	Yb	^1S	4.5396	4.966	4.785	6.254	0.7193	19.93	11.153	8.910
71	Lu	^2D	4.2588	5.412	4.981	6.888	0.6746	29.30	19.455	(16.2)

[a] The ionization potentials for the $6s$ and $4f$ electrons are those given in Refs. [13,15], respectively. The numbers in the parentheses are estimated ones (see Ref. [15]).

culations on Ce, Eu, Gd, Tb, and Yb and obtained the average energies of configurations [3,4,16]. In these calculations, the nucleus is treated as a sphere with a uniform charge distribution. Results on the total energies, ionization energies, and the excitation energies of the ions relative to the ground state of the neutral atoms are summarized in Table III together with those of nonrelativistic RHF calculations with the same GTF's. Okada and Matsuoka [16] calculated the ground state energies of lanthanide atoms with GTF's and the present results are a little lower than those of Okada and Matsuoka, since we employed larger sizes of the basis sets than theirs. Desclaux [4] gave the NHF results with six significant figures. The present results almost fully agree with his (see footnote b in Table III). The total energy differences (Δ) between the nonrelativistic and relativistic calculations are also included in this table. We may see that the relativistic effect (1) lowers the total energies considerably, (2) greatly reduces the 5*d* and 4*f* IP's but slightly increases 5*p* and 6*s* IP's, and (3) always predicts IP's smaller than experiment except for the ionization with the two electron process ($sd \rightarrow \infty f$) in Ce. We note that for 6*s* IP's the relativistic calculations remedy 20–30 % of the error found in the nonrelativistic calculations. We recall that in Ce the ground configuration given by the nonrelativistic HF was $4f^2$. Making a strong contrast, the relativistic HF suggests that the ground configuration should be $5d^1 4f^1$. Since the relativistic calculations are done on the averaged energies of pure spectroscopic states in the *jj* coupling scheme while nonrelativistic calculations are done in pure spectroscopic states in the *LS* coupling scheme, the comparison of the two calculations

TABLE III. Total energies, ionization potentials, and excitation energies of the ions relative to the ground state of the neutral atoms obtained by relativistic and nonrelativistic HF calculations. Δ gives the difference between the two previous columns.

						Total energies			IP's and excitation energies		
Z	State	6*s*	5*p*	5*d*	4*f*	Rel. HF[a,b] (a.u.)	Nonrel. RHF (a.u.)	Δ (a.u.)	Rel. (eV)	Nonrel. (eV)	Expt.[c] (eV)
58 Ce$^+$	^4I	2	5	0	2	−8 860.088 35	−8 566.052 99	294.036 36	26.622	22.300	
58 Ce$^+$	^2D	2	6	1	0	−8 860.702 49	−8 566.330 73	294.371 76	9.911	14.742	(11.5)
58 Ce$^+$	^2G	1	6	1	1	−8 860.891 53	−8 566.707 64[d]	294.183 89[d]	4.766	4.491[d]	7.838
58 Ce$^+$	^2F	2	6	0	1	−8 860.861 18	−8 566.612 19	294.248 99	5.592	7.083	6.678
58 Ce$^+$	^4H	1	6	0	2	−8 860.829 80	−8 566.764 38	294.065 43	6.446	2.942	5.944
58 Ce$^+$	^4H	0	6	2	1	−8 860.879 05	−8 566.743 67	294.135 38	5.106	3.505	5.466
58 Ce	^3H[e]	2	6	0	2	−8 860.992 89	−8 566.919 40	294.073 49	2.009	−1.276	0.590
58 Ce	^1G	2	6	1	1	−8 861.066 70	−8 566.872 50	294.194 20	0.000	0.000	0.000
63 Eu$^+$	^9P	2	5	0	7	−10 845.467 3	−10 422.599 5	422.867 8	27.882	25.669	
63 Eu$^+$	^7F	2	6	0	6	−10 846.292 6	−10 423.068 5	423.224 1	5.426	12.906	(9.76)
63 Eu$^+$	^9S	1	6	0	7	−10 846.317 6	−10 423.381 8	422.935 8	4.746	4.381	5.666
63 Eu	^8S	2	6	0	7	−10 846.492 0	−10 423.542 8	422.949 2	0.000	0.000	0.000
64 Gd$^+$	^{10}F	2	5	1	7	f	−10 819.618 0	f	f	28.381	
64 Gd$^+$	^8G	2	5	0	8	−11 273.166 5	−10 819.662 6	453.503 9	28.588	27.168	
64 Gd$^+$	^8H	2	6	1	6	−11 273.752 6	−10 819.892 4	453.860 2	12.638	20.913	(17.1)
64 Gd$^+$	^8F	1	6	0	8	−11 274.053 2	−10 820.453 8	453.599 4	4.461	5.639	7.132
64 Gd$^+$	^8S	2	6	0	7	−11 274.026 2	−10 820.413 1	453.613 1	5.195	6.745	6.568
64 Gd$^+$	^{10}D	1	6	1	7	−11 274.025 9	−10 820.494 7	453.531 2	5.204	4.525	6.141
64 Gd	$^7\mathrm{F}$[e]	2	6	0	8	−11 274.229 7	−10 820.617 1	453.612 6	−0.343	1.194	1.357
64 Gd	^9D	2	6	1	7	−11 274.217 1	−10 820.661 0	453.556 1	0.000	0.000	0.000
65 Tb$^+$	^7I	2	5	0	9	−11 711.458 7	−11 255.592 1	485.866 6	29.057	26.560	
65 Tb$^+$	^7F	2	6	0	8	−11 712.321 2	−11 226.291 2	486.030 0	5.589	7.537	(6.53)
65 Tb$^+$	^7H	1	6	0	9	−11 712.347 9	−11 226.402 6	485.945 3	4.861	4.505	5.852
65 Tb	^6H	2	6	0	9	−11 712.526 6	−11 226.568 1	485.958 5	0.000	0.000	0.000
70 Yb$^+$	^2P	2	5	0	14	−14 066.448 0	−13 390.330 9	676.117 1	31.195	30.603	
70 Yb$^+$	^2F	2	6	0	13	−14 067.434 6	−13 391.045 8	676.388 8	5.069	11.151	8.910
70 Yb$^+$	^2S	1	6	0	14	−14 067.431 7	−13 391.279 7	676.152 0	5.146	4.784	6.254
70 Yb	^1S	2	6	0	14	−14 067.620 9	−13 391.455 6	676.165 3	0.000	0.000	0.000

[a] The number of the primitive GTF's and their exponents for the respective atoms are the same as that of the nonrelativistic RHF calculations.

[b] The relativistic NHF energies given by Desclaux [4] are 8861.08, 10 846.5, 11 274.2, 11 712.5, and 14 067.7 a.u. for Ce, Eu, Gd, Tb, and Yb, respectively.

[c] The first experimental ionization potentials are those given in Ref. [13]. The excitation energies for the neutral atoms and ions are given in Ref. [14,15], respectively. The numbers in the parentheses are estimated ones (see Ref. [15]).

[d] NHF values.

[e] Excited states in the neutral atoms.

[f] We have failed to get the relativistic solutions.

TABLE IV. Mean value of r, orbital energies, and ionization potentials calculated by relativistic HF and nonrelativistic HF.

				6s				4f			
Z	State			$\langle r \rangle$ (a.u.)	$-\varepsilon$ (eV)	IP (HF) (eV)	IP (expt.)[a] (eV)	$\langle r \rangle$ (a.u.)	$-\varepsilon$ (eV)	IP (HF) (eV)	IP (expt.)[a] (eV)
58	Ce	^1G	non	4.8885	4.664	4.491	7.838	1.0011	19.41	14.742	(11.5)
			rel	4.6486	4.968	4.767	7.838	1.0364[b]	14.73[b]	9.911	(11.5)
								1.0444[c]	14.45[c]		
63	Eu	^8S	non	4.8443	4.653	4.381	5.666	0.8536	19.37	12.906	(9.76)
			rel	4.5883	4.925	4.746	5.666	0.9115[b]	12.15[b]	5.426	(9.76)
								0.9251[c]	11.51[c]		
64	Gd	^9D	non	4.5797	4.990	4.525	6.141	0.7890	28.39	20.916	(17.1)
			rel	4.2759	5.437	5.204	6.141	0.8289[b]	20.11[b]	12.639	(17.1)
								0.8389[c]	19.35[c]		
65	Tb	^6H	non	4.7466	4.748	4.505	5.852	0.8126	18.92	7.537	(6.53)
			rel	4.4795	5.046	4.861	5.852	0.8528[b]	13.13[b]	5.589	(6.53)
								0.8675[c]	12.28[c]		
70	Yb	^1S	non	4.5396	4.966	4.785	6.254	0.7193	19.93	11.153	8.910
			rel	4.2323	5.343	5.146	6.254	0.7433[b]	14.64[b]	5.069	8.910
								0.7616[c]	13.04[c]		

[a] The ionization potentials for the 6s and 4f electrons are those given in Refs. [13,15], respectively. The numbers in the parentheses are estimated ones (see Ref. [15]).

[b] Values for $4f^-$.

[c] Values for $4f^+$.

should be qualitative. We, however, would like to note that the small 4f IP's of the relativistic HF calculations compared with those of experiment are reasonable, since the correlation effects enlarge the IP's given by the HF level approximations.

The mean values of r and the orbital energies for the 6s and 4f orbitals given by the relativistic HF are collected in Table IV together with those of the nonrelativistic ones (RHF). The $\langle r \rangle_{\text{rel}\,6s}$ is less than $\langle r \rangle_{\text{nonrel}\,6s}$ and $\langle r \rangle_{\text{rel}\,4f}$ is greater than $\langle r \rangle_{\text{nonrel}\,4f}$. The absolute value of orbital energies $|\varepsilon_{\text{rel}\,6s}|$ is greater than $|\varepsilon_{\text{nonrel}\,6s}|$ and $|\varepsilon_{\text{rel}\,4f}|$ is smaller than $|\varepsilon_{\text{nonrel}\,4f}|$. These are consistent with the relations between the relativistic and nonrelativistic IP's.

Our conclusions are as follows. In lanthanide atoms, the 4f electrons, which are energetically unstable compared with 5s and 5p electrons, are encircled and protected with these 5s and 5p electrons, suggesting that atomic 4f characteristic is retained in molecules, complexes, and solids. Although the nonrelativistic HF calculations give larger IP's for the 4f electrons, correspondence of the IP's between the nonrelativistic HF calculations and experiment holds fairly well, as we have discussed. We expect that nonrelativistic HF calculations predict the energy levels for molecules well. Inclusion of the relativistic effects mended the larger 4f IP's given in nonrelativistic calculations, giving smaller IP's than experimental ones. The relativistic effects also make the 6s IP's closer to experiments. We finally comment that the well-tempered GTF's always give sufficiently close total energies to those of NHF.

The computer programs used in this study were MCHF72 [17] and ATOMCI [18] for numerical HF and GTF HF, respectively. The program for the relativistic HF was that coded by Okada and Matsuoka [16].

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

---

[1] G. Jeske, H. Lauke, H. Mauermann, H. Schumann, and T. J. Marks, J. Am. Chem. Soc. **107**, 8111 (1985).

[2] C. N. Rao and G. W. Raveau, Acc. Chem. Res. **22**, 106 (1989).

[3] J. P. Desclaux, C. M. Moser, and V. Verhagen, J. Phys. B **4**, 296 (1971).

[4] J. P. Desclaux, At. Data Nucl. Data Tables **12**, 311 (1973).

[5] C. Froese-Fischer, At. Data **4**, 301 (1972); At. Data Nucl. Data Tables **12**, 87 (1973).

[6] J. B. Mann, At. Data Nucl. Data Tables **12**, 1 (1973).

[7] S. Fraga, J. Karwowski, and K. M. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

[8] C. Froese-Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

[9] T. Koga, H. Tatewaki, and A. J. Thakkar, J. Chem. Phys. **100**, 8140 (1994).

[10] H. Tatewaki, T. Koga, Y. Sakai, and A. J. Thakkar, J. Chem. Phys. **101**, 4945 (1994); H. Tatewaki and T. Koga, Chem. Phys. Lett. **228**, 562 (1994).

[11] S. Huzinaga, M. Klobukowski, and H. Tatewaki, Can. J. Chem. **63**, 1812 (1985).

[12] S. Huzinaga and M. Klobukowski, Chem. Phys. Lett. **212**, 260 (1993).

[13] W. C. Martin, L. Hagan, J. Reader, and J. Sugar, J. Phys.

Chem. Ref. Data **3**, 771 (1974).
[14] L. Brewer, J. Opt. Soc. Am. **61**, 1101 (1971).
[15] L. Brewer, J. Opt. Soc. Am. **61**, 1666 (1971).
[16] S. Okada and O. Matsuoka, J. Chem. Phys. **91**, 4193 (1989).
[17] C. Froese-Fischer, Comput. Phys. Commun. **4**, 107 (1972).
[18] F. Sasaki, M. Sekiya, T. Noro, K. Ohtsuki, and Y. Osanai, in *Modern Techniques in Computational Chemistry: MOTECC-91,* edited by E. Clementi (ESCOM Science, Leiden, The Netherlands, 1991), p. 115.