6s and 4f ionized states of lanthanide calculated by the configuration-interaction method

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We have investigated the 6s and 4f ionized states of the whole lanthanide series. It is shown that the calculated 6s ionization energies (IE's) agree with experimental IE's within an error of 0.6 eV, if we add the relativistic correction to those given by configuration-interaction (CI) calculations; 6s IE's by CI calculations with the relativistic correction are in the range of 5.75 (La) to 6.29 eV (Lu); those by experiment are in 5.81 (La) to 6.89 eV (Lu). The relativistic effects reduce 4f IE's by 2–7 eV, and the correlation effects increase those by 1–2 eV for the light lanthanides and by 2–3 eV for the heavy lanthanides. The 4f IE's obtained by CI calculations with the relativistic correction agree with experiment, the error being of $\sim$2 eV throughout the whole lanthanide series. Brewer [J. Opt. Soc. Am. **61**, 1666 (1971)] estimated or assigned 4f ionized states experimentally with the electronic configuration of $4f^{m-1}5d^n6s^2$ ($n=1$ for Ce$^+$, Gd$^+$, and Lu$^+$, and $n=0$ for others). However, for some atoms such as Pr$^+$, Nd$^+$, Pm$^+$, Sm$^+$, and Gd$^+$ we failed to obtain the ionized states having $4f^{m-1}5d^n6s^2$ as the main configuration. [S1050-2947(97)07510-0]

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I. INTRODUCTION

There is considerable current interest in understanding lanthanide chemistry and physics, for example, in the field of catalysis [1] and high-temperature superconductors [2]. Lanthanide elements are characterized by a 4f shell which is gradually filled up from La to Lu. This open shell is responsible for the variety of chemical and physical properties of lanthanides, even though it is localized near the nucleus compared with the 6s and 5d valence shells. The binding energies of localized 4f electrons in the metals are 2–5 eV for Ce to Eu. These levels are closely located near the Fermi level, and 4f holes also lie near the Fermi level [3–7]. In some cases, the electrons and holes in the 4f shell play an important role in showing chemical and physical properties of the lanthanide compounds. For the free lanthanide atoms, 4f ionization energies (IE's) are 7–9 eV, which are only 2–3 eV higher than 6s IE's [8–10]. It would be highly desirable to investigate 4f IE's as well as 6s IE's theoretically for lanthanide atoms.

Recently we investigated the electronic structure of lanthanide atoms with nonrelativistic restricted Hartree-Fock (HF) calculations, where 6s and 4f IE's of the respective atoms are discussed [11]. It is shown that nonrelativistic HF calculations reproduce experimental trends of 6s IE's. However, nonrelativistic HF calculations give larger 4f IE's than those of experiment. If we add the correlation effects, 4f IE's will further increase, and the differences between calculated ones and experiment also increase, since the absolute value of the correlation energies of the neutral atoms is usually larger than those of the ionized atoms. We also performed relativistic HF calculations with well-tempered Gaussian-type functions [12,13] for some selected atoms. The relativistic effects make 6s IE's larger and closer to experiment: those given by experiment are from 5.81 eV for La to 6.89 eV for Lu. On the other hand, the inclusion of the relativistic effects reduces 4f IE's considerably and to below experiment. This result suggests that we have to consider both the correlation and relativistic effects to discuss the 4f ionized states.

In this paper, we analyze the relativistic effects for 6s and 4f ionization energies throughout lanthanides. We also take account of the 6s, 4f, and 5d electron correlations by configuration-interaction (CI) methods. In Sec. II we discuss 6s IE's obtained by CI calculations and those with the relativistic correction. We discuss 4f IE's and characteristics of 4f ionized states of the lanthanide atoms in Sec. III. Concluding remarks are given in Sec. IV.

II. 6S IONIZATION ENERGIES

Before treating the ionized states, we discuss the ground state of Cs, Ba, and La to Lu. It is natural that Cs ($Z=55$) and Ba ($Z=56$) take (Xe core) $4f^1$ or (Xe core) $4f^2$ if we only consider the attractive potential by the Xe-like core. The large Coulomb repulsion between the Xe-like core and 4f electron(s) prevents the electrons from falling in the 4f orbital and makes (Xe core) $6s^1$ or (Xe core) $6s^2$ the ground configuration. The Coulomb repulsion from the Xe-like core makes (Xe core) $5d^16s^2$ the ground configuration for La ($Z=57$) instead of $4f^16s^2$, and $4f^15d^16s^2$ for Ce ($Z=58$) instead of $4f^26s^2$. In order to obtain (Xe core) $4f^m6s^2$, we must wait until Pr ($Z=59$). The complexity comes from the fact that the 4f electrons spread over the region between the Pd-like core ($1s^2$-$4d^{10}$) and the $5s^25p^6$ shell. We may expect that if we ionized a 6s electron, the configurations of $4f^m6s^1$ will be retained, since the ionization of the outermost shell hardly changes the potentials which work on electrons in the inner shells.

The electronic configurations adapted for the ground states are those of the experiment [8,9] (see the fourth col-

TABLE I. $6s$ ionization energies given by nonrelativistic HF (NR,HF) NR HF with relativistic correction ($+\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$), nonrelativistic CI calculations (CI), CI with Davidson Q correction (see Ref. [17]). (CI_{+Q}), Estimate (see footnote a below), and experiment. Units are in eV.

	Ionized								
Z	Atom	State	NRHF	$+\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$	CI	CI_{+Q}	Estimate[a]	Expt.[b]	Others
57	La^+	^3D	4.302	4.53	5.449	5.514	5.75	5.812	
58	Ce^+	$^2G^o$	4.491[c]	4.74	5.322	5.455	5.70	5.866	
59	Pr^+	$^5I^o$	4.254	4.45	4.942	5.045	5.24	5.464	
60	Nd^+	^6I	4.288	4.50	4.949	5.074	5.28	5.525	
61	Pm^+	$^7H^o$	4.321	4.54	4.941	5.086	5.31	5.554	
62	Sm^+	^8F	4.352	4.59	4.932	5.089	5.33	5.644	
63	Eu^+	$^9S^o$	4.381	4.63	4.939	5.107	5.36	5.670	
64	Gd^+	$^{10}D^o$	4.525	4.89	5.249	5.468	5.84	6.150	
65	Tb^+	$^7H^o$	4.505	4.79	4.985	5.166	5.45	5.864	
66	Dy^+	^6I	4.564	4.86	5.000	5.173	5.47	5.939	
67	Ho^+	$^5I^o$	4.621	4.93	5.040	5.212	5.52	6.022	
68	Er^+	^4H	4.677	5.00	5.077	5.250	5.58	6.108	
69	Tm^+	$^3F^o$	4.731	5.08	5.119	5.293	5.64	6.184	
70	Yb^+	^2S	4.784	5.15	5.158	5.329	5.69	6.254	6.34,[d] 5.96[e]
71	Lu^+	^3D	4.980	5.55	5.485	5.723	6.29	6.888	6.90[d]

[a] IE's estimated with $\mathrm{CI}_{+Q}+\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$.

[b] IE's given in Refs. [8,9].

[c] The present program cannot handle this state. The value is taking from the results of numerical HF calculation [11].

[d] IE's obtained by four-component Dirac-Coulomb Fock space CCSD calculations [18].

[e] IE's obtained by multiconfiguration Dirac-Fock with valence-core correlation represented through the core-polarization approach [19].

umn of Table II), and the calculated ionized states are those being deprived of a $6s$ electron. Both configurations are the same as in previous calculations [11]. We have shown $6s$ IE's obtained by previous nonrelativistic HF (NR HF) results and experiment, and shown in Table I and Fig. 1. We see that $6s$ IE's (NR HF) gradually increase from La to Lu with small humps at Ce, Gd, and Lu, as shown in the figure. The difference between experiment and nonrelativistic HF results is 1.5–2 eV.

Using the generalized average energies (GAV's) of configurations [14–16], we performed nonrelativistic and relativistic HF calculations on the ground states and $6s$ ionized states to estimate the relativistic correction. In the relativistic calculations, the nucleus is treated as a sphere with uniform charge distribution. In both HF calculations, we employed well-tempered Gaussian-type functions (GTF's) [12,13], where we augmented six diffuse d's for La through Yb, and two diffuse d's for Lu, since we also investigated the $4f$ ionized states with extra electrons in the $5d$ orbital by the same methods (see Sec. III). The numbers of primitive GTF's are as follows: $(30s,23p,23d,14f)$ for La through Tb; $(29s,22p,22d,13f)$ for Dy through Yb; and $(28s,21p,20d,12f)$ for Lu. These basis sets give the nonrelativistic SCF total energies quite close to those of the numerical HF energies: the differences between the two are 0.0002 (light lanthanides)–0.0016 a.u. (heavy lanthanides).

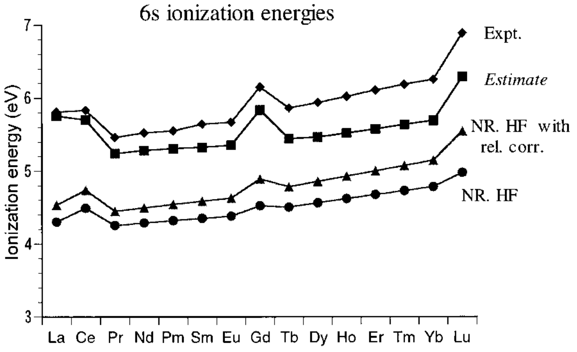

FIG. 1. $6s$ ionization energies (eV) from La to Lu obtained by nonrelativistic HF (●), nonrelativistic HF with the relativistic correction (▲), nonrelativistic CI with the relativistic correction (Estimate, ■), and experiment (◆) [8,9].

The averaged ionization energies for the nonrelativistic and relativistic HF calculations are defined as

$$E_{\mathrm{GAV}}^{\mathrm{IE(NR/Rel)}}=E_{\mathrm{GAV}}^{\mathrm{TE(NR/Rel)}}(\mathrm{Ion})-E_{\mathrm{GAV}}^{\mathrm{TE(NR/Rel)}}(\mathrm{GS}) \tag{1}$$

where $E_{\mathrm{GAV}}^{\mathrm{TE(NR/Rel)}}(\mathrm{Ion/GS})$ is the GAV of the respective HF calculations for the ionized state (Ion) or the ground state (GS). The relativistic correction ($\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$) to IE is as follows:

$$\begin{aligned}\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}&=E_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}-E_{\mathrm{GAV}}^{\mathrm{IE(NR)}}\\&=\{E_{\mathrm{GAV}}^{\mathrm{TE(Rel)}}(\mathrm{Ion})-E_{\mathrm{GAV}}^{\mathrm{TE(Rel)}}(\mathrm{GS})\}\\&\quad-\{E_{\mathrm{GAV}}^{\mathrm{TE(NR)}}(\mathrm{Ion})-E_{\mathrm{GAV}}^{\mathrm{TE(NR)}}(\mathrm{GS})\}\\&=\Delta_{\mathrm{GAV}}^{\mathrm{TE(Rel)}}(\mathrm{Ion})-\Delta_{\mathrm{GAV}}^{\mathrm{TE(Rel)}}(\mathrm{GS}),\end{aligned} \tag{2}$$

where

$$\Delta_{\mathrm{GAV}}^{\mathrm{TE(Rel)}}(\mathrm{Ion/GS})=E_{\mathrm{GAV}}^{\mathrm{TE(Rel)}}(\mathrm{Ion/GS})-E_{\mathrm{GAV}}^{\mathrm{TE(NR)}}(\mathrm{Ion/GS}). \tag{3}$$

Equation (2) shows that the relativistic correction to the IE is equivalent to the difference of the relativistic corrections for the total energies [see Eq. (3)]. The $6s$ IE's with the relativ-

TABLE II. CI total energies (E_{CI}), those with Davidson Q correction (see Ref. [17]) (E_{+Q}), weight (%) of a reference CSF, and correlation energies (E_{corr}) for the ground state.

Z	Atom	State	Configuration	E_{CI} (a.u.)	E_{+Q} (a.u.)	Weight (%)	$E_{\mathrm{corr}}{}^{a}$ (a.u.)
57	La	^2D	$4f^0 5d^1 6s^2$	−8221.117 46	−8221.120 15	91.8	−0.054 00
58	Ce	$^1G^o$	$4f^1 5d^1 6s^2$	−8566.916 03	−8566.921 68	87.2	−0.049 10
59	Pr	$^4I^o$	$4f^3 5d^0 6s^2$	−8921.232 06	−8921.236 16	92.0	−0.055 32
60	Nd	^5I	$4f^4 5d^0 6s^2$	−9283.957 37	−9283.962 73	92.8	−0.079 98
61	Pm	$^6H^o$	$4f^5 5d^0 6s^2$	−9655.206 37	−9655.213 31	93.5	−0.1145
62	Sm	^7F	$4f^6 5d^0 6s^2$	−10 035.0960	−10 035.1043	94.2	−0.1520
63	Eu	$^8S^o$	$4f^7 5d^0 6s^2$	−10 423.7240	−10 423.7336	94.7	−0.1908
64	Gd	$^9D^o$	$4f^7 5d^1 6s^2$	−10 820.8548	−10 820.8662	94.1	−0.2052
65	Tb	$^6H^o$	$4f^9 5d^0 6s^2$	−11 226.8830	−11 226.8995	94.8	−0.3314
66	Dy	^5I	$4f^{10} 5d^0 6s^2$	−11 641.8307	−11 641.8497	95.0	−0.3976
67	Ho	$^4I^o$	$4f^{11} 5d^0 6s^2$	−12 065.7426	−12 065.7652	95.0	−0.4759
68	Er	^3H	$4f^{12} 5d^0 6s^2$	−12 498.6887	−12 498.7159	94.9	−0.5637
69	Tm	$^2F^o$	$4f^{13} 5d^0 6s^2$	−12 940.7937	−12 940.8252	94.9	−0.6514
70	Yb	^1S	$4f^{14} 5d^0 6s^2$	−13 392.1576	−13 392.1930	95.0	−0.7374
71	Lu	^2D	$4f^{14} 5d^1 6s^2$	−13 852.5079	−13 852.5423	95.1	−0.7359

[a] The quantity defined by $E_{+Q} - E_{\mathrm{HF}}$.

istic correction ($\Delta^{\mathrm{IE(Rel)}}_{\mathrm{GAV}}$) are also plotted in Fig. 1. We see that $\Delta^{\mathrm{IE(Rel)}}_{\mathrm{GAV}}$ for $6s$ IE's increases gradually and makes calculated IE's closer to experiment by 0.2–0.4 eV. The remaining errors are still larger than 1.0 eV, and these are expected to arise mainly from the valence electron correlation effects.

We performed single- and double-excitation configuration interaction (SDCI) calculations on the ground and $6s$ ionized states to study correlation effects among $4f$, $5d$, and $6s$ electrons. The HF configuration is taken as the reference one, except for the ground state of La and the $6s$ ionized state of Ce. We used $4f^0 5d^1 6s^2$, $4f^0 5d^2 6s^1$, and $4f^0 5d^3 6s^0$ as the reference functions for the ground state of La, since the results of preliminary calculations give a fairly small weight of 80% for the main configuration ($4f^0 5d^1 6s^2$). Since the state with $4f^1 5d^2 6s^0$ of Ce^+ is lower than the target $6s$ ionized state of $4f^1 5d^1 6s^1$, we add $4f^1 5d^2 6s^0$ as the reference function, and obtain the second lowest solution to obtain a desired state.

We used the same well-tempered GTF's [12,13] as HF calculations and augmented diffuse p, d, and f functions to describe the $6s$-$6s$, $6s$-$4f$, and $6s$-$5d$ electron correlations in the CI calculations. We also augmented eight g and seven h GTF's to describe angular correlation effects. The total numbers of GTF's are ($30s$,$26p$,$23d$,$18f$,$8g$,$7h$) for La through Tb, ($29s$,$25p$,$22d$,$17f$,$8g$,$7h$) for Dy through Yb, and ($28s$,$24p$,$20d$,$17f$,$8g$,$7h$) for Lu. Since we could not perform full SDCI, important configuration state functions (CSF's) were selected by performing the second-order perturbation calculations: generated CSF's for the ground-state range from 8827 of Eu to 236 312 of Ho, and the selected CSF's are from 1502 of Eu to 36 434 of Ho. We performed so-called natural orbital (NO) iterations to obtain compact CI expansions for the ground states as well as for the ionized states, since the SCF atomic orbitals (AO's) usually do not behave as good correlating orbitals. The errors of the correlation energies due to the unselected CSF's are estimated to be 0.0005 a.u. for La through Gd, and 0.001 a.u. for Tb through Lu, and the errors in the IE's are estimated to be less than 0.05 eV for all the lanthanides.

The nonrelativistic SDCI total energies, those with a Davidson correction [17], the weight of the reference functions, and the correlation energies, are collected in Table II. The correlation energies among $4f$, $5d$, and $6s$ electrons gradually increase from La through Lu. The weight of the reference functions is 92% to 95% for Pr through Lu, and it exceeds 90% for La with augmented reference functions of $4f^0 5d^2 6s^1$ and $4f^0 5d^3 6s^0$.

The $6s$ IE's obtained by CI, CI with a Davidson correction (CI_{+Q}), and the estimated IE's with the relativistic correction (Estimate) are shown in Table I, and Estimate's are also plotted in Fig. 1. Nonrelativistic CI results with a Davidson correction reproduce experimental trends fairly well: a gradual increase of the IE's through lanthanides with superimposed on additional IE's at La, Ce, Gd, and Lu. We note that the ground configuration for La, Ce, Gd, and Lu is $4f^m 5d^1 6s^2$ by experiment as well as nonrelativistic HF calculation ($m = 0$, 1, 7, and 14, respectively). The pair-correlation energies between the $5d$ and $6s$ electrons are greater than those between $4f$ and $6s$ electrons, since the mean distance of the $5d$ orbital (~2.5 a.u.) is much larger than the mean distance of the $4f$ orbital (~1 a.u.), and relatively closer to the mean distance of the $6s$ orbital (~5 a.u.). Thus an additional IE comes mainly from the $5d$ and $6s$ correlation effects. The electron correlation effects increase $6s$ IE's by 0.5 to 1.2 eV, which is two times larger than the relativistic correction to $6s$ IE's.

In Table I, we also give the results of $6s$ IE's obtained by the relativistic correlated calculations [18,19]. Eliav, Kaldor, and Ishikawa computed $6s$ IE's of Yb and Lu by the relativistic coupled-cluster (CC) method based on the Dirac-Coulomb Hamiltonian [18]. They simultaneously counted the relativistic effects and the electron correlations among $4d$, $4f$, $5s$, $5p$, $5d$, and $6s$ electrons. The agreement between their $6s$ IE's and experiment is excellent. The difference between their results and ours is ~0.6 eV for both Yb and Lu. Hereafter we discuss this difference of 0.6 eV in detail. Recently, Neogrády *et al.* computed ns IE's of Cu ($Z=29$), Ag ($Z=47$), and Au ($Z=79$), and analyzed their results in the framework of the CC method [20]. They classified the relativistic and correlation effects on IE into three categories: the pure correlation, pure relativistic, and relativistic-correlation contributions. The relativistic-correlation contributions for ns IE's which make IE's larger, are 0.067, 0.131, and 0.337 eV for Cu, Ag, and Au, suggesting that relativistic correlations for Yb ($Z=70$) and Lu ($Z=71$) $6s$ IE's are ~ 0.3 eV. Therefore, we expect that the remaining discrepancy (~ 0.3 eV) between Ref. [18] and the present work comes from the insufficiency of the pure correlation contribution of the present work. Closing this paragraph, we add the result for 6s IE of Yb given by Migdalek and Baylis [19] who used the multi-configuration Dirac-Fock method with a core-polarization. Their result of 5.96 eV is also favorably compared with the experimental value of 6.25 eV.

III. 4*f* IONIZATION ENERGIES

A. HF with relativistic correction

In a previous paper [11], we were concerned with the $4f$ ionized states of $4f^{m-1}5d^{n}6s^{2}$ ($n=1$ for Ce^{+}, Gd^{+}, and Lu^{+}, and $n=0$ for others), where the occupation numbers of valence $5d$ and $6s$ orbitals are those in the ground states. Brewer [10] reported the energy levels of those configuration. We give the results of the nonrelativistic HF calculations [11] with the same spin and angular momentum as Brewer in Table III(a) and Fig. 2(a), where IE's and assignments in the parentheses are experimentally suggested ones [10].

Although calculated IE's by the nonrelativistic HF method are larger than experiment, they simulate the experimental trends quite well: the sudden increases at Gd and Lu are parallel to experiment. We, however, note that the electron correlation effects further enlarge $4f$ IE's, since the correlation energies of the neutral atom are usually greater than those of the ionized atom. The larger $4f$ IE's may be reduced by taking account of the relativistic effects.

In order to estimate the relativistic correction for $4f$ IE's, we performed nonrelativistic and relativistic HF calculations using GAV's of configurations, where we used the same GTF's as for the HF calculations in Sec. II. We introduce the same relativistic correction, $\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$ [see Eq. (2)], for $4f$ IE's as for the case of $6s$ IE's, and give $4f$ IE's with $\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$ in Table III(a) and Fig. 2(a). With the relativistic correction, we find that the calculated $4f$ IE's are always smaller than experiment. We see from Table III(a) and Fig. 2(a) that, for Gd and lighter atoms, calculated IE's with $\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$ agree with experiment within an error of 2.5 eV. However, the discrepancy for heavier atoms than Gd is 4–5 eV, which is considerably larger than the errors for lighter atoms. We consider the correlation effects in the following subsections.

B. MCSCF method with relativistic correction

We infer that if we perform similar CI calculations as for $6s$ IE's and add the relativistic correction to $4f$ IE's, we obtain IE's reasonably close to experiment. However, we met difficulty in the test calculations: the state with unexpected configurations such as $4f^{m-1}5d^{n+1}6s^{1}$ appeared below the assumed target state with $4f^{m-1}5d^{n}6s^{2}$.

We pick out a Nd atom as an example whose ground state is $4f^{4}5d^{0}6s^{2}$ (^{5}I). The observed $4f$ ionized state has been claimed to have $4f^{3}5d^{0}6s^{2}$ ($^{4}I^{o}$) [10]. We performed SDCI with a single reference function of $4f^{3}5d^{0}6s^{2}$ ($^{4}I^{o}$). AO's for CI calculations of the ionized states are composed of the occupied self-consistent field (SCF) orbitals for $4f^{3}5d^{0}6s^{2}$ ($^{4}I^{o}$) and the correlating orbitals (NO's) for the ground state. The CSF selection was performed as it was for the $6s$ IE calculations: the number of CSF's is 14 748, and it is reduced to 2081 by the configuration selection. Although CSF's which have a large matrix element with $4f^{3}5d^{0}6s^{2}$ ($^{4}I^{o}$) are chosen, the state with the configuration $4f^{3}5d^{1}6s^{1}$ becomes the lowest, $4f^{3}5d^{0}6s^{2}$ the second, $4f^{3}5d^{1}6s^{1}$ the third, $4f^{3}5d^{2}6s^{0}$ the fourth, and so on. The IE's of the respective states are 9.99, 10.33, 10.66, and 11.52 eV. The ionized state of $4f^{3}5d^{0}6s^{2}$ ($^{4}I^{o}$) is observed around 8.1 eV above the ground state, and no other lower states with the symmetry ($^{4}I^{o}$) are reported [10]. The calculated lowest state for $^{4}I^{o}$ has the different configuration from experiment, and the corresponding IE is too large.

We therefore perform multiconfiguration SCF (MCSCF) calculations in order to learn the nonrelativistic energy levels of $4f^{m-1}5d^{n}6s^{2}$, $4f^{m-1}5d^{n+1}6s^{1}$, and $4f^{m-1}5d^{n+2}6s^{0}$ with the same symmetry as $4f^{m-1}5d^{n}6s^{2}$ listed in Table III(a). The $4f^{m-1}5d^{n+1}6s^{1}$ and $4f^{m-1}5d^{n+2}6s^{0}$ configurations generate multiple CSF's for the specified symmetries, but $4f^{m-1}5d^{n}6s^{2}$ generates only one. The results are given in Tables III(b) and III(c), and Figs. 2(b) and 2(c).

From Tables III(a)–III(c), we find that the state with the configuration $4f^{m-1}5d^{n+2}6s^{0}$ is the lowest from Ce^{+} to Gd^{+} and Lu^{+}, and that with $4f^{m-1}5d^{n+1}6s^{1}$ is the lowest from Tb^{+} to Yb^{+} in nonrelativistic HF/MCSCF. The state with the configuration $4f^{m-1}5d^{n}6s^{2}$ is always higher than that with $4f^{m-1}5d^{n+1}6s^{1}$ and $4f^{m-1}5d^{n+2}6s^{0}$ in the nonrelativistic level.

Brewer [10] only gave the lowest state arising from each configurations of $4f^{m-1}5d^{n+1}6s^{1}$ and $4f^{m-1}5d^{n+2}6s^{0}$, all of which have different symmetries from what we study. Therefore we have no experimental IE's of $4f^{m-1}5d^{n+1}6s^{1}$ and $4f^{m-1}5d^{n+2}6s^{0}$ with the same symmetry discussed in the present work. We give IE's of the symmetry given by Brewer denoted as Expt. in Tables III(b) and III(c) and Figs. 2(b) and 2(c). We note that these IE's (Expt.) are lower limits of IE's of the symmetry of the present calculations. Brewer reported that the state arising from $4f^{m-1}5d^{n}6s^{2}$ is the lowest for Ho^{+} through Yb^{+} among the states arising from $4f^{m-1}5d^{n}6s^{2}$, $4f^{m-1}5d^{n+1}6s^{1}$, and $4f^{m-1}5d^{n+2}6s^{0}$. However, the results of nonrelativistic HF/MCSCF calculations are not consistent with experiment.

We add the relativistic correction to IE's, $\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$, for $4f^{m-1}5d^{n+1}6s^{1}$ and $4f^{m-1}5d^{n+2}6s^{0}$ configuration in the same manner as the case of $4f^{m-1}5d^{n}6s^{2}$. The IE's with $\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$ are summarized in Tables III(b) and III(c) and Figs. 2(b) and 2(c). The relativistic effects reduce the IE's considerably, and make the state with the configuration $4f^{m-1}5d^{n+2}6s^{0}$ the lowest for Ce^{+}, that with $4f^{m-1}5d^{n+1}6s^{1}$ the lowest from Pr^{+} to Dy^{+}, and that with

TABLE III. (a) $4f$ ionization energies from $4f^m5d^n6s^2$ to $4f^{m-1}5d^n6s^2$ given by nonrelativistic HF (NR HF), NR HF with relativistic correction $(+\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}})$, and experiment. Units are in eV. (b) $4f$ ionization energies from $4f^m5d^n6s^2$ to $4f^{m-1}5d^{n+1}6s^1$ given by nonrelativistic MCSCF (NR MCSCF), NR MCSCF with relativistic correction $(+\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}})$, and experiment. Units are in eV. (c) $4f$ ionization energies from $4f^m5d^n6s^2$ to $4f^{m-1}5d^{n+2}6s^0$ given by nonrelativistic MCSCF (NR MCSCF), NR MCSCF with relativistic correction $(+\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}})$, and experiment. Units are in eV.

Atom	Ionized configuration	State	NR HF/MCSCF IE's (eV)	$+\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$ IE's (eV)	Expt.[a] State	Expt.[a] IE's (eV)
			(a)			
Ce^+	$4f^05d^16s^2$	^2D	14.742	10.572	$(^2D_{5/2})$	11.808
Pr^+	$4f^25d^06s^2$	^3H	9.800	6.035	$(^3H_4)$	(7.4)
Na^+	$4f^35d^06s^2$	$^4I^o$	9.881	5.952	$(^4I^o_{9/2})$	(8.9)
Pm^+	$4f^45d^06s^2$	^5I	9.870	5.764	$(^5I_4)$	(7.7)
Sm^+	$4f^55d^06s^2$	$^6H^o$	11.139	6.844	$(^6H^o_{5/2})$	(8.6)
Eu^+	$4f^65d^06s^2$	^7F	12.905	8.413	$(^7F_0)$	(9.8)
Go^+	$4f^65d^16s^2$	^8H	20.913	15.619	$(^8H_{3/2})$	(17.1)
Tb^+	$4f^85d^06s^2$	^7F	7.537	2.625	$^7F_6$	6.595
Dy^+	$4f^95d^06s^2$	$^6H^o$	8.822	3.687	$^6H^o_{15/2}$	7.468
Ho^+	$4f^{10}5d^06s^2$	^5I	8.484	3.121	$(^5I_8)$	(7.3)
Er^+	$4f^{11}5d^06s^2$	$^4I^o$	8.102	2.506	$^4I^o_{15/2}$	6.954
Tm^+	$4f^{12}5d^06s^2$	^3H	9.315	3.478	$^3H_6$	7.729
Yb^+	$4f^{13}5d^06s^2$	$^2F^o$	11.150	5.670	$^2F^o_{7/2}$	8.910
Lu^+	$4f^{13}5d^16s^2$	$^3H^o$	19.450	12.432	$(^3F^o_2)$	(16.2)
			(b)			
Ce^+	$4f^05d^26s^1$	^2D	12.142	9.155	$^4F_{5/2}$	10.159
Pr^+	$4f^25d^16s^1$	^3H	7.247	4.607	$^5I_4$	6.435
Nd^+	$4f^35d^16s^1$	$^4I^o$	7.870	5.116	$^6K^o_{9/2}$	6.927
Pm^+	$4f^45d^16s^1$	^5I	8.133	5.254	$(^7L_5)$	(6.9)
Sm^+	$4f^55d^16s^1$	$^6H^o$	9.347	6.335	$(^8F^o_{3/2})$	8.310
Eu^+	$4f^65d^16s^1$	^7F	11.331	8.179	$^9D_2$	9.414
Gd^+	$4f^65d^26s^1$	^8H	18.056	14.302	$(^{10}I_{3/2})$	(15.7)
Tb^+	$4f^85d^16s^1$	^7F	5.801	2.351	$^9G_7$	6.265
Dy^+	$4f^95d^16s^1$	$^6H^o$	6.909	3.298	$^8H^o_{17/2}$	7.252
Ho^+	$4f^{10}5d^16s^1$	^5I	7.110	3.336	$(^7K_9)$	(7.4)
Er^+	$4f^{11}5d^16s^1$	$^4I^o$	7.238	3.298	$(^6K^o_{13/2})$	7.430
Tm^+	$4f^{12}5d^16s^1$	^3H	8.612	4.500	$J=5$[b]	8.239
Yb^+	$4f^{13}5d^16s^1$	$^2F^o$	10.699	6.411	$(^4G^o_{5/2})$	9.572
Lu^+	$4f^{13}5d^26s^1$	$^3H^o$	17.473	12.521	$(^5H^o_4)$	(16.0)
			(c)			
Ce^+	$4f^05d^36s^0$	^2D	10.798	8.758	$(^4F_{3/2})$	(10.4)
Pr^+	$4f^25d^26s^0$	^3H	6.770	5.015	$^5L_6$	6.190
Nd^+	$4f^35d^26s^0$	$^4I^o$	7.297	5.467	$^6M^o_{13/2}$	6.669
Pm^+	$4f^45d^26s^0$	^5I	7.435	5.521	$(^7M_6)$	(6.7)
Sm^+	$4f^55d^26s^0$	$^6H^o$	8.664	6.660	$(^8L^o_{9/2})$	(8.0)
Eu^+	$4f^65d^26s^0$	^7F	10.604	8.505	$^9P_3$	10.212
Gd^+	$4f^65d^36s^0$	^8H	17.252	14.728	$(^{10}I_{3/2})$	(16.1)
Tb^+	$4f^85d^26s^0$	^7F	6.106	3.804	$^9G_7$	6.968
Dy^+	$4f^95d^26s^0$	$^6H^o$	7.616	5.204	$(^8K^o_{17/2})$	(8.3)
Ho^+	$4f^{10}5d^26s^0$	^5I	7.558	5.034	$(^7L_{10})$	(8.9)
Er^+	$4f^{11}5d^26s^0$	$^4I^o$	7.442	4.805	$J=13/2$[b]	9.042
Tm^+	$4f^{12}5d^26s^0$	^3H	8.826	6.071	$J=4$[b]	10.008
Yb^+	$4f^{13}5d^26s^0$	$^2F^o$	10.982	8.108	$J=5/2$[b]	11.835
Lu^+	$4f^{13}5d^36s^0$	$^3H^o$	17.142	13.850	$(^5H^o_4)$	(17.5)

[a] IE's are given in Refs. [8,10]. IE's in the parentheses are estimated ones, and assignments in the parentheses are suggested ones (see Ref. [10]).

[b] The total angular momentum J is given in Ref. [8].

$4f^{m-1}5d^n6s^2$ the lowest from Ho^+ to Lu^+. The relativistic effects reverse the order of IE's and give similar trends as experiment: for example, the state with the configuration $4f^{m-1}5d^n6s^2$ is the lowest $4f$ ionized state among the three configurations for the heavy atoms from Ho^+ to Yb^+.

Let us discuss the relativistic effects for $4f$ ionizations in detail. We show the relativistic correction $\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$ for $4f^{m-1}5d^n6s^2$, $4f^{m-1}5d^{n+1}6s^1$, and $4f^{m-1}5d^{n+2}6s^0$ con-

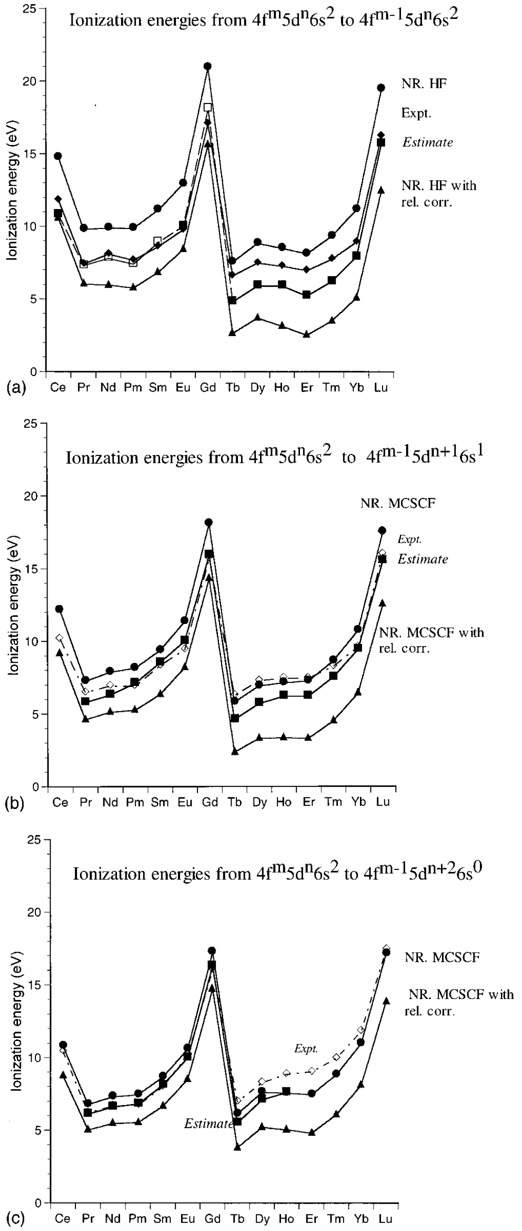

FIG. 2. (a) $4f$ ionization energies (eV) from $4f^m5d^n6s^2$ to $4f^{m-1}5d^n6s^2$, where m and n are the occupation numbers of $4f$ and $5d$ orbitals for the ground state as shown in Table II: nonrelativistic HF (●); nonrelativistic HF with the relativistic correction (▲); experiment (◆) [8,10]; and nonrelativistic CI with the relativistic correction, noted as Estimate (■ or □), where □ means the state not having $4f^{m-1}5d^n6s^2$ as a leading configuration. (b) $4f$ ionization energies (eV) from $4f^m5d^n6s^2$ to $4f^{m-1}5d^{n+1}6s^1$, where m and n are the occupation numbers of $4f$ and $5d$ orbitals for the ground state as shown in Table II: nonrelativistic MCSCF (●); nonrelativistic MCSCF with the relativistic correction (▲), nonrelativistic CI with the relativistic correction, noted as Estimate (■) and Expt. (◇), which are taken from the IE's from the ground state to the lowest state of $4f^{m-1}5d^{n+1}6s^1$ [8,10]. (c) $4f$ ionization energies (eV) from $4f^m5d^n6s^2$ to $4f^{m-1}5d^{n+2}6s^0$, where m and n are the occupation numbers of $4f$ and $5d$ orbitals for the ground state as shown in Table II: nonrelativistic MCSCF (●); nonrelativistic MCSCF with the relativistic correction (▲); nonrelativistic CI with the relativistic correction, noted as Estimate (■), and Expt. (◇), which are taken from the IE's from the ground state to the lowest state of $4f^{m-1}5d^{n+2}6s^0$ [8,10].

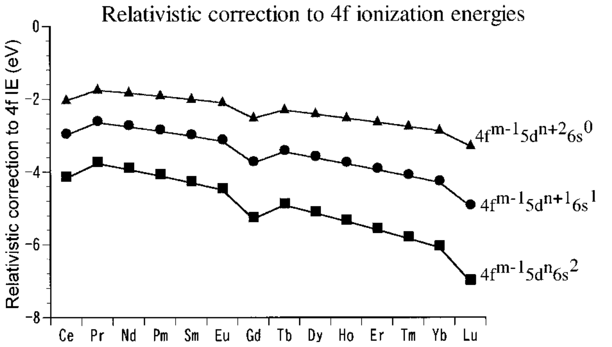

FIG. 3. The relativistic correction for $4f$ ionization energies from $4f^m5d^n6s^2$ to $4f^{m-1}5d^n6s^2$ (■), $4f^{m-1}5d^{n+1}6s^1$ (●), and $4f^{m-1}5d^{n+2}6s^0$ (▲), where m and n are the occupation numbers of $4f$ and $5d$ orbitals for the ground state as shown in Table II.

figurations in Fig. 3. The relativistic correction for all the $4f$ ionized states is negative and quite large, from -2 to -7 eV: the correction is the largest for $4f^{m-1}5d^n6s^2$, followed by $4f^{m-1}5d^{n+1}6s^1$, and the correction for $4f^{m-1}5d^{n+2}6s^0$ is the smallest. It gradually increases in magnitude from light atoms to heavy atoms. We see that the relativistic effects rearrange the energetic order of the states, since these effects are as large as the energy difference among the states arising from $4f^{m-1}5d^n6s^2$, $4f^{m-1}5d^{n+1}6s^1$, and $4f^{m-1}5d^{n+2}6s^0$ obtained by nonrelativistic HF calculations.

The $6s$ and $5d$ orbital energies of the $4f^{m-1}5d^{n+1}6s^1$ ionized states obtained by the GAV HF calculations are shown in Fig. 4. We see that the $6s$ orbital energies are always higher than the $5d$ orbital energies in the case of nonrelativistic HF calculations. The relativistic effects reduce the $6s$ orbital energies and increase the $5d$ orbital energies. These effects make $6s$ more stable than $5d$ for the heavier atoms than Er$^+$. The relativistic effects, thus, make the states arising from $4f^{m-1}5d^{n+1}6s^1$ more unstable than $4f^{m-1}5d^n6s^2$ for heavier atoms, and give energetic orders of $4f$ ionized states that are the same as those of experiment. However, inclusion of the relativistic effects makes $4f$ IE's too small compared with experiment, especially for heavy atoms. We need to consider the electron correlation effects to obtain better agreement with experiment.

C. 4*f* IE's given by multireference SDCI

We performed multireference SDCI (MRSDCI) calculations for the $4f$ ionized states through Ce$^+$ to Lu$^+$. Referring the results of MCSCF, we employ $4f^{m-1}5d^n6s^2$, $4f^{m-1}5d^{n+1}6s^1$, and $4f^{m-1}5d^{n+2}6s^0$ as the reference functions for Pr$^+$ through Lu$^+$, except for Ce$^+$ and Gd$^+$. We use $4f^05d^16s^2$, $4f^05d^26s^1$, $4f^05d^36s^0$, $4f^25d^06s^1$, $4f^25d^16s^0$, $4f^15d^06s^16p^1$, and $4f^15d^16s^06p^1$ to reference CSF's for Ce$^+$ and $4f^65d^16s^2$, $4f^65d^26s^1$, $4f^65d^36s^0$, and $4f^85d^16s^0$ for Gd$^+$, since they are lower than the states observed in experiment.

It is hard to perform SDCI calculations for $4f$ IE's in the same scheme as $6s$ IE's, since we use the plural reference functions given above and the huge set of correlating orbitals. We reduce the number of AO's in the following way.

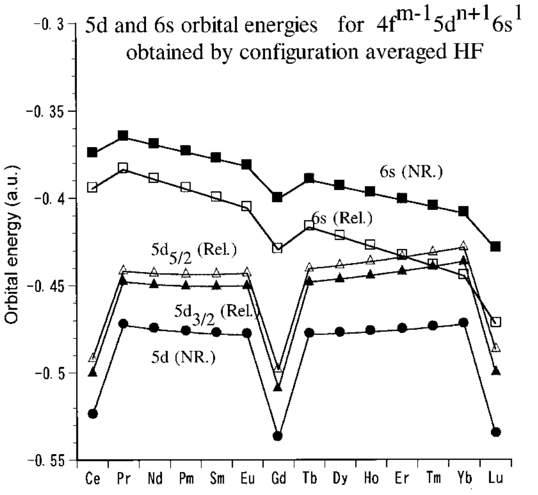

FIG. 4. The orbital energies (a.u.) of $6s$ and $5d$ for $4f^{m-1}5d^{n+1}6s^1$ ($n=1$ for Ce^+, Gd^+, and Lu^+, and $n=0$ for others) obtained by the relativistic HF and nonrelativistic HF calculations using the generalized average energies of configurations.

(a) We determine $1s$-$6s$, $2p$-$5p$, $3d$-$4d$, and $4f$ occupied orbitals by the SCF calculation on $4f^{m-1}5d^n6s^2$. The $5d$ orbital is determined by the SCF calculation on $4f^{m-1}5d^n6s^2$ for Ce^+, Gd^+, and Lu^+, and for others by the MCSCF calculation on $4f^{m-1}5d^{n+1}6s^1$.

(b) We select important correlating orbitals (one s type, two p types, two d types, two f types, two g types) from the NO's of the ground states, and these orbitals are orthogonalized to the occupied orbitals given above. These numbers of correlating orbitals are determined by choosing the NO's with the occupation numbers greater than 0.001 for the CI calculation on the ground state of Dy.

We performed SDCI calculations with selected CSF's for the ionized states using the above AO sets to get the correlation energies among $4f$, $5d$, and $6s$ electrons. The ground states are also recalculated with the reduced AO sets constructed in the same manner. The number of CSF's generated for the $4f$ ionized states is between 474 (Ce^+) and 144 624 (Dy^+), and the number of the selected CSF's is between 330 (Ce^+) and 15 486 (Dy^+). The errors of final CI calculations relative to those without the selection are estimated to be 0.001 a.u. for Ce^+ through Eu^+, and they are in the range of 0.005–0.01 a.u. for Gd^+ through Lu^+. The errors relative to the results without the CSF selection in $4f$ IE's are of the order of ~0.1 eV for Ce^+ through Eu^+, and 0.2 eV for Gd^+ through Lu^+.

As we have shown in the previous subsections, the relativistic correction is quite important to predict the relative energies of the states with $4f^{m-1}5d^n6s^2$, $4f^{m-1}5d^{n+1}6s^1$, and $4f^{m-1}5d^{n+2}6s^0$. We estimate the relativistic correction as follows.

(a) Summing up weights for the reference CSF's that belong to each of $4f^{m-1}5d^n6s^2$, $4f^{m-1}5d^{n+1}6s^1$, and $4f^{m-1}5d^{n+2}6s^0$ configurations, we calculate the relative weights for the each configurations and renormalize them.

(b) Multiplying the relativistic correction $\Delta_{\mathrm{GAV}}^{\mathrm{IE(Rel)}}$ [see Eq. (2) and Fig. 3], with the renormalized weights given in (a) and summing them up, we obtain the relativistic correction for the respective states. Adding this correction to the results of CI, we obtain IE's with the relativistic correction, which are denoted as ''Estimate'' in Table IV and Figs. 2(a)–2(c).

Since we could not obtain the solutions for Pr^+, Nd^+, Pm^+, Sm^+, and Gd^+ with the character of $4f^{m-1}5d^n6s^2$, we give the solutions which have a considerable but not sufficiently large enough weight of $4f^{m-1}5d^n6s^2$ in Table IV. We see from Table IV and Figs. 2(a)–2(c) that the correlation effects increase $4f$ IE's by about 2 eV for the light atoms and 3 eV for the heavy atoms, and make them closer to experiment. The valence electron correlation effects as well as the relativistic effects are quite important to discuss the $4f$ ionized states.

Estimate gives the state of $4f^{m-1}5d^{n+2}6s^0$ or $4f^{m-1}5d^{n+1}6s^1$ the lowest for Pr^+ to Dy^+ and that of $4f^{m-1}5d^n6s^2$ the lowest from Ho^+ to Yb^+. For Ho^+ through Yb^+, the results are consistent with experiment. Estimate agrees with experiment, the errors being of ~2 eV through lanthanides.

We recall that the relativistic-correlation contribution [20] is around 0.3 eV for the $6s$ IE of Au, indicating that the coupling between the relativistic and correlation effects is larger in the ground state than in the $6s$ ionized state. The magnitude of the contribution for the $4f$ IE is not clear. Ishikawa and Koc [21] performed the relativistic and nonrelativistic many-body perturbation theory calculations, and gave the pair correlation energies for the ground state of Hg. They showed that relativistic-correlation couplings increase the correlation energies by 0.203 a.u. for Hg, and the sum of $4f$-nl pair-correlation energies is around one-third of those. If the orbitals are not changed in the $4f$ ionization process, their analysis suggest that the coupling effects increase $4f$ IE by about 0.2 eV. These contributions for $4f$ IE's of the heavy lanthanides are expected to be smaller than this, indicating that the pure correlation correction is responsible for the errors of Estimate, ~2 eV, given in the last paragraph.

We now summarize the calculation, using Fig. 2(a). The differences between Estimate and experiment for the last half of the lanthanides are slightly large compared with those of the lighter atoms than Gd. For the first half atoms of lanthanides, all $4f$ electrons have the same spin, but the last half lanthanides have antiparallel spin pairs. The correlation effects, therefore, are expected to be more important for the last half atoms.

States where $4f^{m-1}5d^n6s^2$ is predominant do not exist for the light lanthanide atoms (Pr^+–Sm^+). We give detailed results for Nd^+ in Table V as a typical example of these ions. The sum of the weights over this configuration up to the 15th is greater than 85%, showing that $4f^35d^06s^2$ is smeared out among these 15 states. The same story holds for Gd^+ of $4f^65d^16s^2$ to which experiment give the IE of 17.1 eV, since we again cannot find the solution with $4f^65d^16s^2$ as a main one up to the 20th solution.

D. Discussion of $4f$ ionized states

We summarize what we calculated. For the neutral lanthanide, the states with $6s^2$ are usually more stable than those with $6s^1$, where a $6s$ electron is excited to the inner orbitals, such as $5d$ or $4f$ orbitals. When the inner $4f$ electron is removed, the state arising from $4f^{m-1}5d^n6s^2$ becomes unstable compared with the states of $4f^{m-1}5d^{n+1}6s^1$

TABLE IV. Ionization energies given by MRSDCI, MRSDCI with relativistic correction (estimate) (see text), and experiment.

Ionized		Nth	Leading		CI	Estimate[a]	Expt.[b]	
Atom	State	solution	configuration	Weight (%)	IE's (eV)	IE's (eV)	State	IE's (eV)
Ce$^+$	^2D	17[c]	$4f^05d^16s^2$	73.1	15.009	10.8	$(^2D_{5/2})$	11.808
Pr$^+$	^3H	1	$4f^25d^26s^0$	89.3	7.843	6.1	$^5L_6$	6.190
		2	$4f^25d^16s^1$	69.4	8.085	5.8	$^5I_4$	6.435
		13[d]	$(4f^25d^06s^2)^{\text{e}}$	39.4	(9.901)	(7.3)	$(^3H_4)$	(7.4)
Nd$^+$	$^4I^o$	1	$4f^35d^26s^0$	83.2	8.431	6.6	$^6M^o_{13/2}$	6.669
		3	$4f^35d^16s^1$	87.0	8.910	6.3	$^6K^o_{9/2}$	6.927
		7[f]	$(4f^35d^06s^2)^{\text{e}}$	18.0	(9.968)	(7.8)	$(^4I^o_{9/2})$	(8.9)
Pm$^+$	^5I	1	$4f^45d^26s^0$	81.5	8.793	6.8	$(^7M_6)$	(6.7)
		3	$4f^45d^16s^1$	59.9	9.504	7.1	$(^7L_5)$	(6.9)
		7[g]	$(4f^45d^06s^2)^{\text{e}}$	42.8	(10.306)	(7.4)	$(^5I_4)$	(7.7)
Sm$^+$	$^6H^o$	1	$4f^55d^26s^0$	84.5	10.133	8.1	$(^8L^o_{9/2})$	(8.0)
		3	$4f^55d^16s^1$	48.9	10.877	8.5	$(^8F^o_{3/2})$	8.310
		7[h]	$(4f^55d^06s^2)^{\text{e}}$	13.2	(11.707)	(8.9)	$(^6H^o_{5/2})$	(8.6)
Eu$^+$	^7F	1	$4f^65d^26s^0$	86.2	12.086	10.0	$^9P_3$	10.212
		2	$4f^65d^16s^1$	58.6	12.647	10.0	$^9D_2$	9.414
		6	$4f^65d^06s^2$	55.8	13.643	10.0	$(^7F_0)$	(9.8)
Gd$^{+\text{i}}$	^8H	2	$4f^65d^36s^0$	90.8	18.974	16.3	$(^{10}I_{3/2})$	(16.1)
		3	$4f^65d^26s^1$	83.6	19.379	15.9	$(^{10}I_{3/2})$	(15.7)
		12[j]	$(4f^65d^16s^2)^{\text{e}}$	15.9	(21.674)	(18.1)	$(^8H_{3/2})$	(17.1)
Tb$^+$	^7F	1	$4f^85d^16s^1$	84.5	7.711	4.6	$^9G_7$	6.265
		2	$4f^85d^26s^0$	48.7	8.192	5.5	$(^9G_7)$	6.968
		4	$4f^85d^06s^2$	71.1	8.978	4.8	$^7F_6$	6.595
Dy$^+$	$^6H^o$	1	$4f^95d^16s^1$	91.1	8.975	5.7	$^8H^o_{17/2}$	7.252
		2	$4f^95d^26s^0$	50.7	9.961	7.1	$(^8K^o_{17/2})$	(8.3)
		5	$4f^95d^06s^2$	77.3	10.474	5.9	$^6H^o_{15/2}$	7.468
Ho$^+$	^5I	1	$4f^{10}5d^16s^1$	86.3	9.285	6.2	$(^7K_9)$	(7.4)
		3	$4f^{10}5d^26s^0$	66.6	10.236	7.6	$(^7L_{10})$	(8.9)
		4	$4f^{10}5d^06s^2$	79.2	10.305	5.9	$(^5I_8)$	(7.3)
Er$^+$	$^4I^o$	1	$4f^{11}5d^16s^1$	96.6	9.880	6.2	$(^6K^o_{13/2})$	7.430
		2	$4f^{11}5d^06s^2$	85.1	10.451	5.2	$^4I^o_{15/2}$	6.954
Tm$^+$	^3H	1	$4f^{12}5d^16s^1$	95.5	11.326	7.5	$J=5^{\text{k}}$	8.239
		2	$4f^{12}5d^06s^2$	88.8	11.786	6.2	$^3H_6$	7.729
Yb$^+$	$^2F^o$	1	$4f^{13}5d^16s^1$	91.2	13.459	9.4	$(^4G^o_{5/2})$	9.572
		2	$4f^{13}5d^06s^2$	90.1	13.738	7.9	$^2F^0_{7/2}$	8.910
Lu$^+$	$^3H^o$	1	$4f^{13}5d^26s^1$	96.0	20.185	15.5	$(^5H^o_4)$	(16.0)
		4	$4f^{13}5d^16s^2$	69.8	22.024	15.7	$(^3F^o_2)$	(16.2)

[a] See text.

[b] IE's are given in Refs. [8,10]. IE's in the parentheses are estimated ones, and assignments in the parentheses are suggested ones (see Ref. [10]).

[c] The lower states obtained by CI calculation are not included, since the occupied orbitals employed are only suitable for this state. Resulting total energies for lower states are extremely high comparing with those obtained by the CI calculation, which uses suitable HF orbitals for the respective states.

[d] The leading configuration for this state is $4f^25d^26s^0$, whose weight is 49.0%.

[e] The solution is having a considerable weight of $4f^m5d^n6s^2$, but not large enough as a leading configuration.

[f] The leading configuration for this state is $4f^35d^26s^0$, whose weight is 73.3%.

[g] The leading configuration for this state is $4f^45d^26s^0$, whose weight is 45.5%.

[h] The leading configuration for this state is $4f^55d^26s^0$, whose weight is 59.6%.

[i] The lowest state, having a $4f^85d^06s^1$ configuration obtained by CI calculation, is not included, since the occupied orbitals employed are only suitable for the states listed in this table. The resulting IE for $4f^85d^06s^1$ is extremely high compared with that of experiments [8,10].

[j] The leading configuration for this state is $4f^65d^36s^0$, whose weight is 52.0%.

[k] The total angular momentum J is given in Ref. [8].

TABLE V. Ionization energies (eV), weight (%) of reference CSF's for Nd obtained by MRSDCI calculation. Estimate's are given by MRSDCI with relativistic correction (see text).

Nth solution	IE's (eV)		Weight (%)		
	MRSDCI	Estimate	$4f^3 5d^0 6s^2$	$4f^3 5d^1 6s^1$	$4f^3 5d^2 6s^0$
1	8.431	5.6	0.1	13.1	83.2
2	8.775	5.8	0.0	22.4	74.1
3	8.910	5.1	0.0	87.0	5.4
4	9.241	6.3	0.0	16.5	73.6
5	9.468	6.7	1.8	4.3	89.1
6	9.589	6.4	1.7	33.1	54.5
7	9.968	6.8	18.0	3.0	73.3
8	10.069	7.3	2.1	1.8	92.5
9	10.096	6.8	20.2	2.5	72.2
10	10.559	6.8	0.1	87.1	7.7
11	10.597	7.7	1.7	9.5	63.3
12	10.724	8.0	0.2	3.8	73.7
13	10.798	7.1	30.9	5.1	50.2
14	10.872	7.7	8.6	8.9	52.0
15	10.972	7.2	0.2	75.7	8.2

or $4f^{m-1}5d^{n+2}6s^0$ in the nonrelativistic level. We see that $4f^{m-1}5d^{n+2}6s^0$ is the lowest for lighter atoms. As the nuclear charge increases, it is expected that the $5d$ electrons are pulled in and the repulsion energies between Xe-like core and $5d$ electrons and those between the $4f$ and $5d$ electrons increase. The ionized states with $4f^{m-1}5d^{n+1}6s^1$ thus become the lowest. The atoms heavier than Gd ''prefer'' the $4f^{m-1}5d^{n+1}6s^1$ configuration to the $4f^{m-1}5d^{n+2}6s^0$ configuration in the nonrelativistic level (see Table IV). For heavier atoms, the relativistic effects make the states arising from $4f^{m-1}5d^{n}6s^2$ more stable than those from $4f^{m-1}5d^{n+1}6s^1$, as discussed in Sec. II. We classify $4f$ ionized states into three categories.

(1) $4f$ ionization is accompanied with $6s^2 \rightarrow 5d^2$ deexcitation because of the strong attractive force constructed by the Xe-like core with $m-1$ $4f$ electrons: Pr^+–Sm^+ with $4f^{m-1}5d^{n+2}6s^0$.

(2) $4f$ ionization is accompanied with $6s \rightarrow 5d$ deexcitation because of the not-so-strong attractive force of the ion core: Eu^+–Dy^+ with $4f^{m-1}5d^{n+1}6s^1$.

(3) No deexcitation occurs because of the stabilization due to the relativistic effects: Ho^+–Yb^+, with $4f^{m-1}5d^{n}6s^2$.

IV. CONCLUDING REMARKS

In lanthanide atoms, the relativistic effects and the correlation effects enlarge $6s$ IE's. The relativistic-correlation couplings are also indispensable for investigating $6s$ IE's quantitatively.

Nonrelativistic HF/MCSCF calculations give larger IE's for the $4f$ electrons than experiment. The relativistic effects reduce $4f$ IE's considerably: about 2–3 eV for $4f^{m-1}5d^{n+2}6s^0$, 3–4 eV for $4f^{m-1}5d^{n+1}6s^1$, and 4–7 eV for $4f^{m-1}5d^{n}6s^2$. The correlation effects increase the IE's by about 1–2 eV for the light lanthanides and by about 2–3 eV for the heavy lanthanides. The remaining errors in $4f$ IE's come mainly from the insufficiency of the electron correlation effects.

The $4f$ ionized states having the configuration of $4f^{m-1}5d^{n}6s^2$ ($n=1$ for Ce^+, Gd^+, and Lu^+, and $n=0$ for others) with the specified symmetry is assigned or estimated by Brewer [10]. We obtained the state having this configuration with the specified symmetry [8,10] as the main one for Ce^+, Eu^+, Tb^+, Dy^+, Ho^+, Er^+, Tm^+, Yb^+, and Lu^+. However, we failed to obtain the solution with this as the main one for Pr^+, Nd^+, Pm^+, Sm^+, and Gd^+, where the target configuration is smeared out over certain CI manifolds.

The computer program used in this study was ATOMCI [22] for nonrelativistic HF, MCSCF, and CI. Okada and Matsuoka's program was used for the relativistic HF calculations [16].

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