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Energy differences between $4f^{n+1}5d^0 6s^2$ and $4f^n 5d^1 6s^2$ electron configurations for the lanthanide atoms

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We study the energy difference $\Delta E(n)$ between the $4f^{n+1}5d^0 6s^2$ and $4f^n 5d^1 6s^2$ configurations of the entire neutral lanthanide series, where n runs from 0 (La) through 13 (Yb). The $\Delta E(n)$ values obtained by numerical multiconfigurational Dirac-Fock (MC-DF) calculations are lower than experiment, while those given by nonrelativistic self-consistent-field (NR-SCF) calculations are larger than experiment. The difference between the MC-DF and NR-SCF $\Delta E(n)$ values is about 3–5 eV. If we add the correlation energy corrections obtained by nonrelativistic second-order perturbation calculations to $\Delta E(n)$ given by MC-DF calculations, the resulting values of $\Delta E(n)$ for the neutral lanthanides agree with experiment to within 1.0 eV, except for La and Yb.

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I. INTRODUCTION

Since 1960, there has been much study of the energy differences of low-lying electronic configurations of lanthanide atoms and ions in order to determine the lowest states of the neutral, singly ionized, and doubly ionized atoms [1–7]. The energy difference of $4f^n 5d^1 6s^m - 4f^{n+1}5d^0 6s^m$ ($m=2$, 1, and 0) is generally called the system difference and will be denoted as $\Delta E(n)$:

$$\Delta E(n) = E_{\text{total}}(4f^n 5d^1 6s^m) - E_{\text{total}}(4f^{n+1}5d^0 6s^m). \quad (1)$$

Here E_{total} is the total energy of the lowest state of the specified configuration. A positive value of $\Delta E(n)$ implies that $4f^{n+1}5d^0 6s^m$ is the ground state, and a negative value of $\Delta E(n)$ implies $4f^n 5d^1 6s^m$ is the ground state.

Figure 1 shows experimental values of $\Delta E(n)$ plotted against n for the three series $m=2$, 1, and 0, which correspond to neutral, singly ionized, and doubly ionized lanthanide atoms. All data are taken from Ref. [1]. In Fig. 1. filled rectangle data points represent observed values and open rectangles show estimated values. We observe that the three lines are parallel to each other and that the first half of the lanthanide series of atoms has a similar $\Delta E(n)$ pattern to the second half. It is known that the experimental $4f$ ionization energies (IEs) of doubly ionized states, $E_{\text{total}}(4f^n) - E_{\text{total}}(4f^{n+1})$, have a similar pattern to Fig. 1 [4], indicating that the binding energy of $5d$ electrons is almost constant throughout the lanthanide elements.

The interaction between the electrons of a given configuration is often expressed in terms of the Slater-Condon parameters F^k. Racah gave a combination of new parameters in terms of F^k for the f shell, where the expression for the energy is separated into spin and angular-momentum terms. The expression for the energy difference ($4f^n - 4f^{n+1}$) is

$$U_f - nE^0 - N(S_n, S_{n+1})E^1 - M(L_n, L_{n+1})E^3, \quad (2)$$

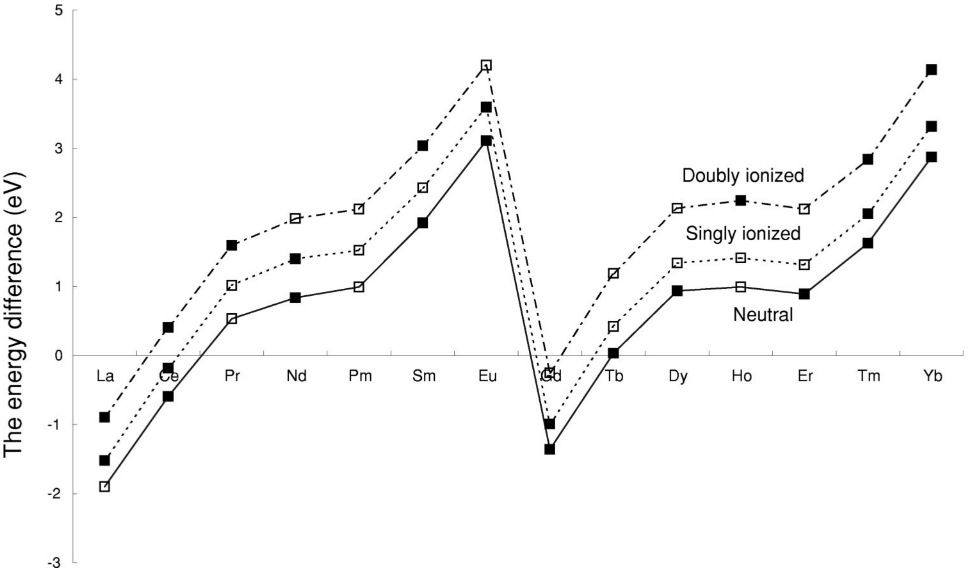

FIG. 1. The energy difference $\Delta E(n)$ for the neutral, singly ionized, and doubly ionized lanthanide atoms given by Ref. [1].

TABLE I. The coefficients of Racah parameters for the ionization energies of doubly ionized $4f^{n+1}$ lanthanide atoms [see Eq. (2)].

Atom	n	$N(S_n,S_{n+1})$	$M(L_n,L_{n+1})$
La	0	0	0
Ce	1	0	-9
Pr	2	0	-12
Nd	3	0	0
Pm	4	0	12
Sm	5	0	9
Eu	6	0	0
Gd	7	9	0
Tb	8	9	-9
Dy	9	9	-12
Ho	10	9	0
Er	11	9	12
Tm	12	9	9
Yb	13	9	0

where U_f, E^0, E^1, and E^3 are Racah parameters [8]. The functions $N(S_n,S_{n+1})$ and $M(L_n,L_{n+1})$ are dependent on the Russell-Saunders quantum numbers S and L of the $4f^n$ and $4f^{n+1}$ electronic configurations. If we choose the LS coupling term given by Hund's rule for the lowest states of each configuration, then $N(S_n,S_{n+1})$ and $M(L_n,L_{n+1})$ take the values listed in Table I. The term $[U_f - nE^0]$ increases smoothly across the series, when U_f is constant and E^0 is negative. The gap between Eu and Gd is explained by the third term, $-9E^1$. The irregularities at the quarter and three-quarter points are due to the terms in E^3. If we suppose that U_f, E^0, E^1, and E^3 are constant, we now see why the curves for the first half and the second half of the lanthanide series of atoms are similar.

Several authors [4–7] have estimated the energy difference $\Delta E(n)$ based on the work of Racah [8], with the assumption that the interaction between the outer electrons and $4f$ electrons varies smoothly from element to element. The values of the parameters are successively calculated to estimate the unknown $\Delta E(n)$ values.

In previous papers [9,10], we have discussed the $4f$ ionization energies of the neutral lanthanide atoms. We found that relativistic effects reduce the $4f$ ionization energies by 2–7 eV and that correlation effects increase them by 1–2 eV for the first half of the lanthanides and by 2–3 eV for the second half. Both effects are therefore significant in investigating the difference $\Delta E(n)$ for lanthanide atoms.

In this paper we systematically analyze the relativistic and correlation effects in the difference $\Delta E(n)$ of the neutral lanthanide atoms. In Sec. II we study $\Delta E(n)$ values obtained by nonrelativistic self-consistent-field (NR-SCF) and numerical multiconfigurational Dirac-Fock (MC-DF) calculations. In Sec. III we investigate the $6s$, $4f$, and $5d$ electron correlation effects using second-order Rayleigh-Schrödinger (RS) and Brillouin-Wigner (BW) perturbation theory. We also discuss the importance of $5s$ and $5p$ core correlation effects on $\Delta E(n)$. Concluding remarks are set out in Sec. IV.

II. NR-SCF AND MC-DF CALCULATIONS

To study $\Delta E(n)$ for the neutral lanthanide atoms, we performed NR-SCF and MC-DF calculations on states generated from the $4f^{n+1}5d^06s^2$ and $4f^n5d^16s^2$ configurations. For the NR-SCF calculations, we used well-tempered Gaussian-type functions (GTFs) [11,12]. We added six diffuse d GTFs to La through Yb, in order to investigate states with a single electron excitation to the $5d$ orbital. The numbers of primitive GTFs are as follows: $(30s,23p,23d,14f)$

TABLE II. Total energies for $4f^{n+1}5d^06s^2$ and $4f^n5d^16s^2$ and the energy difference $\Delta E(n)$ obtained by NR-SCF calculations. LS terms are assigned by experiment [13] except for Ho, Er, Tm, and Yb.

		Total energies (a.u.)				
Atom	n	^{2S+1}L	$4f^{n+1}5d^06s^2$	^{2S+1}L	$4f^n5d^16s^2$	$\Delta E(n)$ (eV)
La	0	^2F	$-8\,221.063\,6$	^2D	$-8\,221.066\,5$	-0.079
Ce	1	^3H	$-8\,566.919\,4$	^1G	$-8\,566.872\,5$	1.276
Pr	2	^4I	$-8\,921.180\,8$	^4I	$-8\,921.073\,7$	2.913
Nd	3	^5I	$-9\,283.882\,8$	^5L	$-9\,283.775\,3$	2.924
Pm	4	^6H	$-9\,655.098\,8$	$^6D^a$	$-9\,654.997\,4$	2.759
Sm	5	^7F	$-10\,034.952\,4$	^7H	$-10\,034.789\,7$	4.427
Eu	6	^8S	$-10\,423.542\,8$	^8D	$-10\,423.321\,9$	6.010
Gd	7	^7F	$-10\,820.617\,1$	^9D	$-10\,820.661\,0$	-1.195
Tb	8	^6H	$-11\,226.568\,2$	^8G	$-11\,226.551\,4$	0.457
Dy	9	^5I	$-11\,641.452\,2$	^7H	$-11\,641.386\,3$	1.793
Ho	10	^4I	$-12\,065.289\,4$	$^6I^a$	$-12\,065.217\,7$	1.950
Er	11	^3H	$-12\,498.152\,3$	$^5G^a$	$-12\,498.086\,1$	1.801
Tm	12	^2F	$-12\,940.173\,9$	$^4F^a$	$-12\,940.070\,2$	2.821
Yb	13	^1S	$-13\,391.455\,7$	$^3P^a$	$-13\,391.286\,7$	4.598

[a] No experimental assignments are available. The lowest LS term was determined by NR-SCF calculations.

TABLE III. Total energies for $4f^{n+1}5d^06s^2$ and $4f^n5d^16s^2$ and the energy difference $\Delta E(n)$ obtained by MC-DF calculations.

			Total energies (a.u.)			
Atom	n	J	$4f^{n+1}5d^06s^2$	J	$4f^n5d^16s^2$	$\Delta E(n)$ (eV)
La	0	5/2	−8 493.545 7	3/2	−8 493.647 0	−2.754
Ce	1	4	−8 861.042 8	4	−8 861.096 9	−1.470
Pr	2	9/2	−9 238.267 3	9/2	−9 238.276 3	−0.243
Nd	3	4	−9 625.314 3	6	−9 625.330 2	−0.435
Pm	4	5/2	−10 022.328 0	11/2[a]	−10 022.355 6	−0.7513
Sm	5	0	−10 429.480 4	2	−10 429.454 8	0.711
Eu	6	7/2	−10 846.946 2	3/2	−10 846.889 0	1.556
Gd	7	6	−11 274.577 9	2	−11 274.746 1	−4.576
Tb	8	15/2	−11 712.815 9	13/2	−11 712.927 1	−3.024
Dy	9	8	−12 161.777 0	8	−12 161.853 3	−2.078
Ho	10	15/2	−12 621.572 3	17/2	−12 621.657 1	−2.307
Er	11	6	−13 092.351 3	6	−13 092.455 1	−2.827
Tm	12	7/2	−13 574.325 8	9/2	−13 574.403 3	−2.109
Yb	13	0	−14 067.671 7	2	−14 067.698 1	−0.720

[a] J value is given by Hund's rule.

for La through Tb, and ($29s$,$22p$,$22d$,$13f$) for Dy through Yb. These basis sets yield SCF total energies quite close to the numerical HF energies for the state arising from $4f^{n+1}5d^06s^2$ and $4f^n5d^16s^2$; the difference in the total energies is less than 7×10^{-4} a.u. In calculating the lowest state of each configuration, we employed the experimental LS specification [13] where it is available. Since no experimental LS assignment is available for the $4f^n5d^16s^2$ configuration of Pm, Ho, Er, Tm, and Yb, we performed the NR-SCF calculations for all possible LS coupling terms and then picked out the lowest level. The LS values for those atoms calculated by NR-SCF are summarized in Table II, together with the NR-SCF total energies and $\Delta E(n)$ values.

We also performed numerical MC-DF calculations using the GRASP2 package [14]. The program generates all possible configuration state functions with the target J value corresponding to a nonrelativistic electronic configuration like $4f^{n+1}5d^06s^2$ or $4f^n5d^16s^2$. We used the experimentally assigned J values of the lowest state of each configuration, except for Pm with configuration $4f^n5d^16s^2$, where we used the $J=11/2$ according to Hund's rule for Pm. The J values for Ho, Er, Tm, and Yb having configuration $4f^n5d^16s^2$ according to experiment, are consistent with the LS values shown in Table II.

The total energies and $\Delta E(n)$ values for the neutral lanthanide atoms calculated by MC-DF are listed in Table III. By comparing Tables II and III, we see that the inclusion of relativistic effects lowers the total electronic energies considerably; the reduction varies from 272 a.u. for La to 675 a.u. for Yb. The $\Delta E(n)$ values for the neutral lanthanide atoms

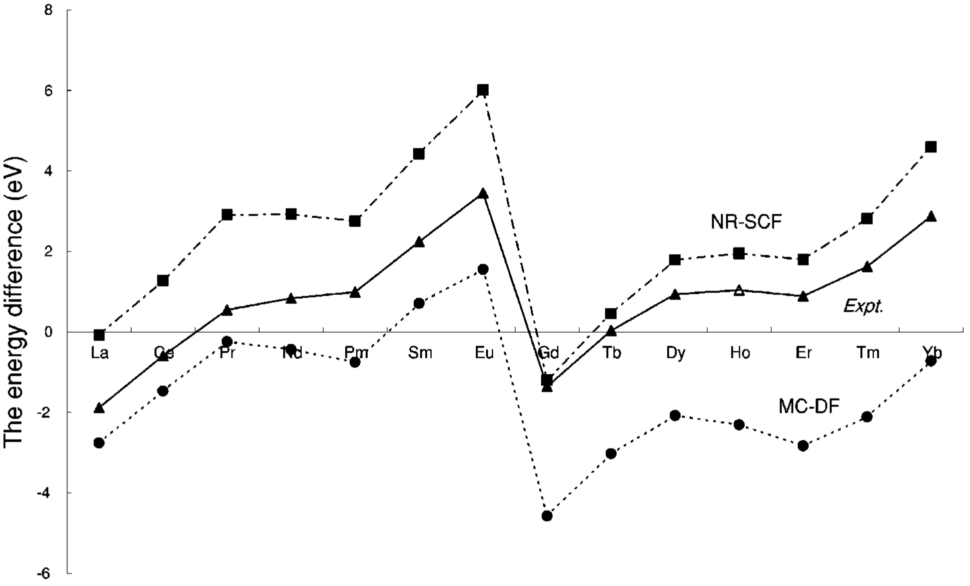

FIG. 2. The energy difference $\Delta E(n)$ obtained by NR-SCF, MC-DF, and experiment [13].

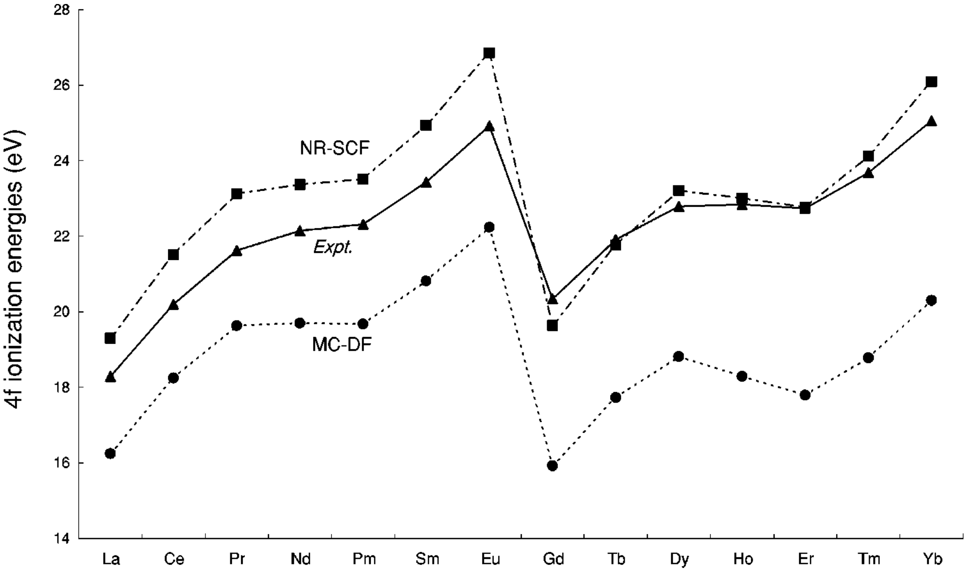

FIG. 3. The $4f$ ionization energies for $4f^{n+1}5d^06s^0$ obtained by NR-SCF, MC-DF, and experiment [13].

determined by NR-SCF and MC-DF calculations are also shown in Fig. 2, together with experimental $\Delta E(n)$ values [13]. The $\Delta E(n)$ values from MC-DF calculations are smaller than those found experimentally, while values from the NR-SCF calculations are larger than the experimental values. The values of $\Delta E(n)$ obtained by MC-DF and NR-SCF differ by about 3–5 eV. This is consistent with our previous studies [9,10] of $4f$ IE, where experimental $4f$ IE values are located centrally between those obtained by NR-SCF and relativistic SCF calculations; the relativistic corrections to the excitations from $4f$ to $5d$ have the same tendency as the ionizations. The discrepancy between experiment and MC-DF $\Delta E(n)$ values might be reduced by including electron correlation effects.

To clarify whether the decrease in the number of $4f$ electrons or the increase in the number of $5d$ electrons determines the shape of $\Delta E(n)$, we calculated the $4f$ IEs of $4f^{n+1}5d^06s^0$ and $5d$ IEs of $4f^n5d^16s^0$ by NR-SCF and MC-DF calculations. The results are shown in Figs. 3 and 4. The $4f$ IEs for doubly ionized lanthanide atoms have a similar n dependence to those of $\Delta E(n)$ shown in Fig. 2. On the other hand, the $5d$ IEs slowly oscillate with the occupation number n of the $4f$ orbital. The radial expectation values of $\langle r_{5d}\rangle$ for $4f^n5d^16s^0$ and $\langle r_{4f}\rangle$ for $4f^{n+1}5d^06s^0$ obtained by NR-SCF calculations are plotted in Fig. 5. The values of $\langle r_{5d}\rangle$ for $4f^n5d^16s^0$ also oscillate slowly. There is a correlation between $5d$ IEs and $\langle r_{5d}\rangle$ values, since an electron is more easily ionized when farther from the nucleus than near it (see Figs. 4 and 5). This simple description is appropriate only for an electron outside the inner $4f$ shell, which has a complicated electronic structure. Ionization from the inner $4f$ core requires separate consideration. In contrast to $\langle r_{5d}\rangle$, the values of $\langle r_{4f}\rangle$ for $4f^{n+1}5d^06s^0$ gradually decrease with the increasing occupation number n of the $4f$ orbital. The $4f$ IEs cannot be explained so simply. They are strongly related to the electronic structure of the $4f$ core, as shown by formula (2).

We have shown that the $\Delta E(n)$ values of the neutral lan-

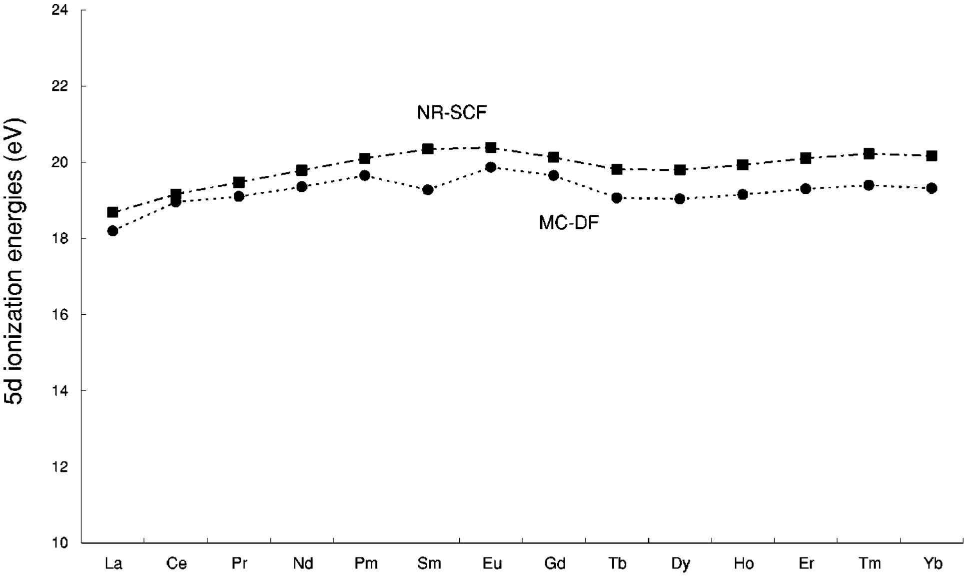

FIG. 4. The $5d$ ionization energies for $4f^n5d^16s^0$ obtained by NR-SCF and MC-DF.

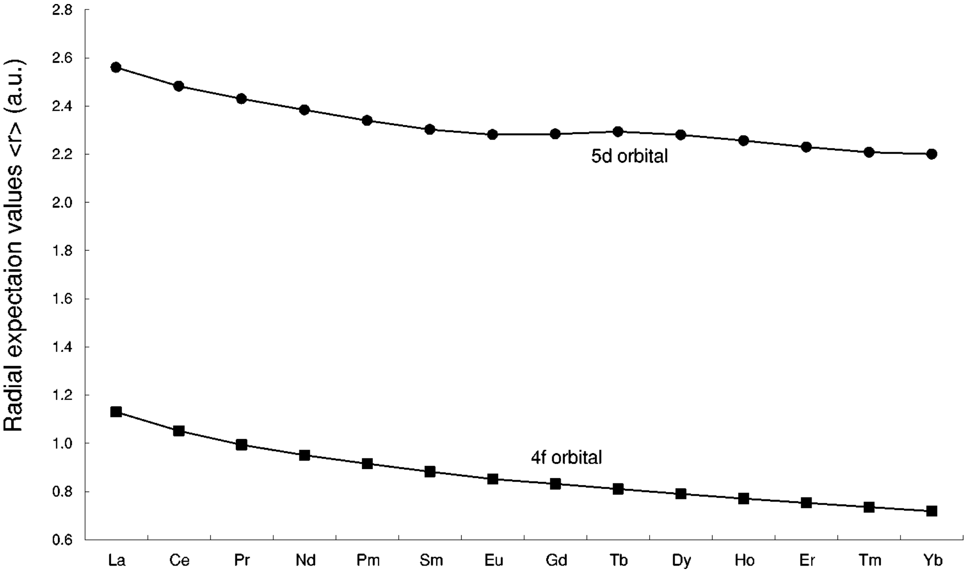

FIG. 5. Radial expectation values $\langle r_{5d}\rangle$ for $4f^n5d^16s^0$ and $\langle r_{4f}\rangle$ for $4f^{n+1}5d^06s^0$ obtained by NR-SCF.

thanide atoms parallel the $4f$ IEs of doubly ionized atoms ($4f^{n+1}5d^06s^0$), but not the $5d$ IEs of doubly ionized atoms ($4f^n5d^16s^0$). We therefore conclude that the structure of $\Delta E(n)$ is determined principally by changes in the $4f$ shell electronic structure and not by the $5d$ occupation.

III. CORRELATION EFFECTS

We have to consider the electron correlation effects to analyze the discrepancy between experiments and results obtained by MC-DF calculations. However, it is quite difficult to calculate the electron correlation effects for the lanthanides atoms especially on the second half elements. To simplify a complicated calculation of the electronic correlation effects, we introduce the following assumptions: (1) a weak coupling between relativistic and nonrelativistic correlation effects and (2) the correspondence between LS (nonrelativistic) and JJ (relativistic) terms. Then we simply add the difference in nonrelativistic correlation energies $[\Delta E^{\mathrm{val}}_{\mathrm{corr}} = E^{\mathrm{val}}_{\mathrm{corr}}(4f^n5d^16s^2) - E^{\mathrm{val}}_{\mathrm{corr}}(4f^{n+1}5d^06s^2)]$ to the energy difference $\Delta E(n)$ given by MC-DF calculations.

We now comment on the first assumption. Ishikawa and Koc [15] calculated the second-order correlation energies for Xe ($Z=54$) and Hg ($Z=80$) by a many-body perturbation theory, using the nonrelativistic and Dirac-Coulomb Hamiltonian. They have shown that the difference of the correlation energies calculated with the two Hamiltonians is about 1.3% and 4.0% of the total correlation energy for Xe and Hg, respectively. So far as the Dirac-Coulomb Hamiltonian is used, the coupling between the relativistic effects and the correlation effects is small for the atoms with $Z \leqslant 80$. Actually for the cases of the $6s$ and $4f$ ionizations of the lanthanide atoms [10], where the first assumption was imposed, the ionization potentials were found to be close to experiment. The second assumption is rationalized, if we follow the experimental assignment [13]; for the target JJ states arising from $4f^{n+1}5d^06s^2$, the weight of the leading LS term is quite large ($\geqslant$89%), except for La and Tm and for the JJ states arising from $4f^n5d^16s^2$ that is in a range of 55–92 %.

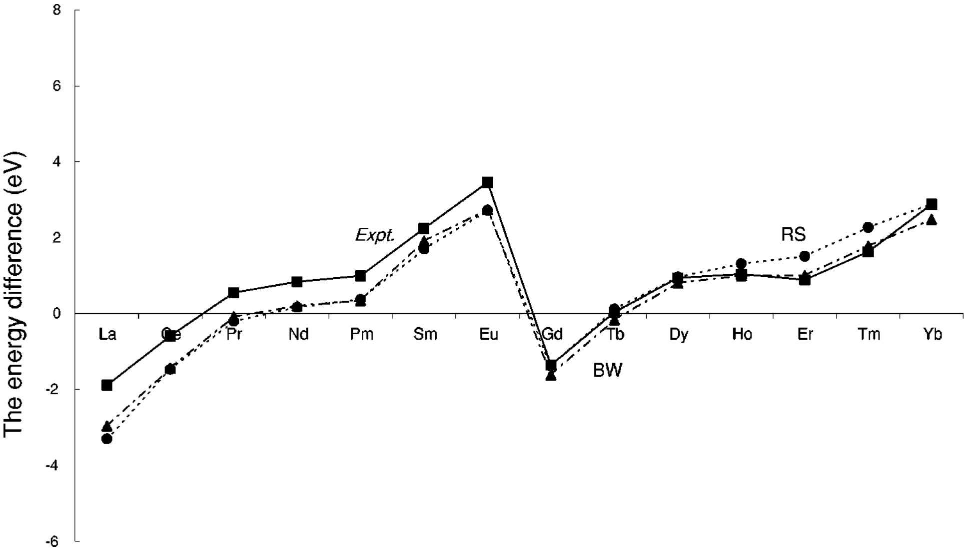

FIG. 6. The energy difference $\Delta E(n)$ given by MC-DF corrected with $\Delta E^{\mathrm{val}}_{\mathrm{corr}}$ obtained by RS and BW calculations and experiment [13]; correlation effects among $4f$, $5d$, and $6s$ are included.

TABLE IV. Correlation energies for $4f^{n+1}5d^{0}6s^{2}$ and $4f^{n}5d^{1}6s^{2}$ obtained by RS calculations among $4f$, $5d$, and $6s$ electrons, the correlation energy difference $\Delta E_{\mathrm{corr}}^{\mathrm{val}}$, the energy difference $\Delta E(n)$ given by MC-DF corrected by RS correlation energies, and experimental $\Delta E(n)$ values.

		Correlation energies (eV)			$\Delta E(n)$ (eV)	
Atom	n	$4f^{n}5d^{1}6s^{2}$	$4f^{n+1}5d^{0}6s^{2}$	$\Delta E_{\mathrm{corr}}^{\mathrm{val}}$	Corrected	Expt.[a]
La	0	−1.734	−1.186	−0.548	−3.302	−1.884
Ce	1	−1.535	−1.540	0.005	−1.465	−0.591
Pr	2	−2.073	−2.112	0.038	−0.205	0.550
Nd	3	−2.551	−3.154	0.603	0.168	0.839
Pm	4	−3.550	−4.672	1.122	0.371	0.992
Sm	5	−5.345	−6.332	0.987	1.698	2.241
Eu	6	−6.693	−7.853	1.160	2.716	3.453
Gd	7	−8.476	−11.671	3.195	−1.381	−1.357
Tb	8	−11.678	−14.816	3.138	0.114	0.035
Dy	9	−14.448	−17.486	3.037	0.959	0.938
Ho	10	−17.161	−20.784	3.622	1.315	1.039
Er	11	−21.181	−25.518	4.337	1.510	0.890
Tm	12	−25.268	−29.646	4.378	2.269	1.627
Yb	13	−28.963	−32.571	3.608	2.888	2.875

[a]See Ref. [13].

We performed nonrelativistic second-order RS and BW perturbation calculations to estimate the correlation energies. Generally the second-order theory gives larger correlation energies than the exact one in their absolute values. We, however, do not necessarily need to calculate the exact correlation energies, when the energy differences among the states are considered. The greater part of the errors (overestimated correlation energies) would cancel with each other because we consider the excitation energies of the valence-like excited states.

Two types of electron correlations are considered: first, among the $4f$, $5d$, and $6s$ electrons; and second, among the $4f$, $5s$, $5p$, $5d$, and $6s$ electrons. We used the well-tempered GTFs [11,12] in the SCF calculations together with eight g and seven h GTFs to describe the angular correlation effect. The basis sets are $(30s,26p,23d,18f,8g,7h)/[19s,18p,17d,15f,8g,7h]$ for La–Tb and $(29s,25p,22d,17f,8g,7h)/[19s,18p,17d,15f,8g,7h]$ for Dy–Yb, using the general contraction scheme [16].

The valence correlation energies $E_{\mathrm{corr}}^{\mathrm{val}}$ for $4f^{n+1}5d^{0}6s^{2}$ and $4f^{n}5d^{1}6s^{2}$ will be discussed, together with the differ-

TABLE V. Correlation energies for $4f^{n+1}5d^{0}6s^{2}$ and $4f^{n}5d^{1}6s^{2}$ obtained by BW calculations among $4f$, $5d$, and $6s$ electrons, the correlation energy difference $\Delta E_{\mathrm{corr}}^{\mathrm{val}}$, the energy difference $\Delta E(n)$ given by MC-DF corrected by BW correlation energies, and experimental $\Delta E(n)$ values.

		Correlation energies (eV)			$\Delta E(n)$ (eV)	
Atom	n	$4f^{n}5d^{1}6s^{2}$	$4f^{n+1}5d^{0}6s^{2}$	$\Delta E_{\mathrm{corr}}^{\mathrm{val}}$	Corrected	Expt.[a]
La	0	−1.224	−1.016	−0.208	−2.962	−1.884
Ce	1	−1.294	−1.331	0.037	−1.433	−0.591
Pr	2	−1.690	−1.850	0.161	−0.082	0.550
Nd	3	−2.183	−2.819	0.636	0.201	0.839
Pm	4	−3.115	−4.212	1.097	0.346	0.992
Sm	5	−4.560	−5.758	1.198	1.909	2.241
Eu	6	−6.006	−7.189	1.184	2.740	3.453
Gd	7	−7.645	−10.609	2.964	−1.612	−1.357
Tb	8	−10.600	−13.464	2.864	−0.160	0.035
Dy	9	−13.023	−15.907	2.885	0.807	0.938
Ho	10	−15.561	−18.865	3.304	0.997	1.039
Er	11	−19.193	−23.026	3.833	1.006	0.890
Tm	12	−22.794	−26.677	3.884	1.775	1.627
Yb	13	−26.235	−29.437	3.202	2.482	2.875

[a]See Ref. [13].

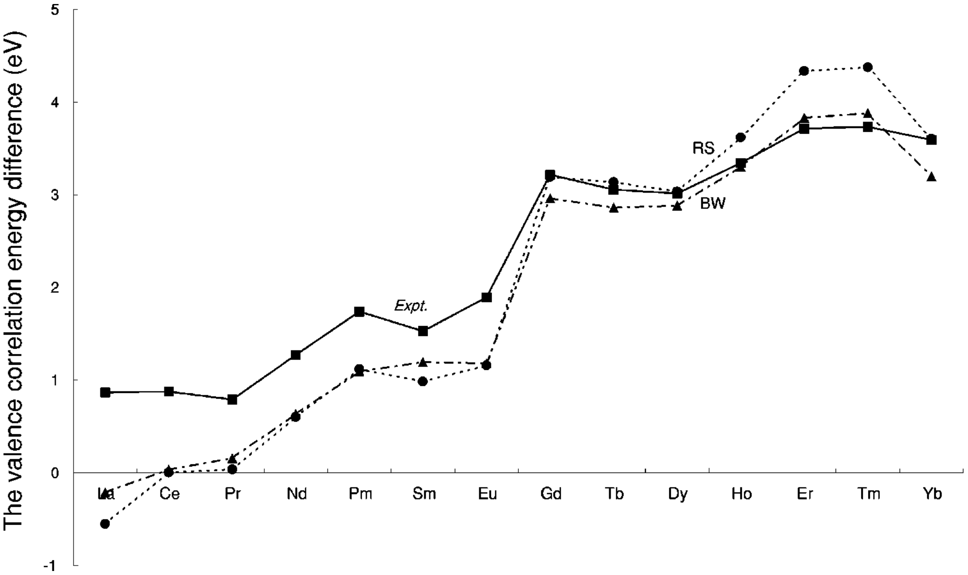

FIG. 7. The valence $4f$, $5d$, and $6s$ correlation energy difference $\Delta E_{\text{corr}}^{\text{val}}$ between $4f^{n+1}5d^{0}6s^{2}$ and $4f^{n}5d^{1}6s^{2}$ obtained by valence RS and BW calculations and $\Delta E_{\text{corr}}^{\text{expt}}$ [see Eq. (3)].

ence in these correlation energies $\Delta E_{\text{corr}}^{\text{val}}$ and the energy difference $\Delta E(n)$ given by MC-DF calculations modified with $\Delta E_{\text{corr}}^{\text{val}}$. The results obtained by RS and BW calculations for the valence $4f$, $5d$, and $6s$ electron correlation are shown in Tables IV and V, together with experimental $\Delta E(n)$ values.

We also show the energy difference $\Delta E(n)$ in Fig. 6. We see from Tables IV and V and Fig. 6 that $\Delta E(n)$, modified with $\Delta E_{\text{corr}}^{\text{val}}$ and assuming additivity of the relativistic and correlation effects, agrees with experiment. The values of $\Delta E_{\text{corr}}^{\text{val}}$ calculated by RS and BW are shown in Fig. 7, together with $\Delta E_{\text{corr}}^{\text{expt}}$ calculated as

$$\Delta E_{\text{corr}}^{\text{expt}} = \Delta E(n)^{\text{expt}} - \Delta E(n)^{\text{MC-DF}}. \tag{3}$$

The absolute value of the calculated correlation energies of $4f^{n+1}5d^{0}6s^{2}$ is greater than for $4f^{n}5d^{1}6s^{2}$, except for La, indicating that $\Delta E(n)$ is increased by valence correlation effects. For example, the RS calculation increase $\Delta E(n)$ by $0-1.3$ eV for the first half of the lanthanide series and by 3.0–4.5 eV for the second half. The calculated correlation energies are close to the experimental values, showing the importance of correlation effects among the $4f$, $5d$, and $6s$ electrons in the overall energy differences.

We now discuss correlation effects among the $5s$, $5p$, and valence electrons. Tables VI and VII show correlation energies, the correlation correction ($\Delta E_{\text{corr}}^{\text{core}}$), modified $\Delta E(n)$ values with $\Delta E_{\text{corr}}^{\text{core}}$ obtained by RS and BW calculations, and experimental values of $\Delta E(n)$. Modified and ex-

TABLE VI. Correlation energies for $4f^{n+1}5d^{0}6s^{2}$ and $4f^{n}5d^{1}6s^{2}$ obtained by RS calculations including $4f$, $5s$, $5p$, $5d$, and $6s$ electrons, the correlation energy difference $\Delta E_{\text{corr}}^{\text{core}}$, the energy difference $\Delta E(n)$ given by MC-DF corrected by RS correlation energies, and experimental $\Delta E(n)$ values.

		Correlation energies (eV)			$\Delta E(n)$ (eV)	
Atom	n	$4f^{n}5d^{1}6s^{2}$	$4f^{n+1}5d^{0}6s^{2}$	$\Delta E_{\text{corr}}^{\text{core}}$	Corrected	Expt.[a]
La	0	−9.597	−11.629	2.032	−0.722	−1.884
Ce	1	−12.099	−12.765	0.665	−0.805	−0.591
Pr	2	−13.605	−14.111	0.507	0.264	0.550
Nd	3	−14.844	−16.296	1.452	1.017	0.839
Pm	4	−16.441	−18.596	2.155	1.404	0.992
Sm	5	−19.010	−21.009	1.999	2.710	2.241
Eu	6	−20.740	−22.715	1.976	3.532	3.453
Gd	7	−23.173	−27.894	4.720	0.144	−1.357
Tb	8	−27.216	−31.344	4.128	1.104	0.035
Dy	9	−30.244	−33.733	3.489	1.411	0.938
Ho	10	−33.280	−36.968	3.689	1.382	1.039
Er	11	−38.014	−42.432	4.418	1.591	0.890
Tm	12	−42.813	−46.835	4.022	1.913	1.627
Yb	13	−46.839	−49.066	2.228	1.508	2.875

[a] See Ref. [13].

TABLE VII. Correlation energies for $4f^{n+1}5d^06s^2$ and $4f^n5d^16s^2$ obtained by BW calculations including $4f$, $5s$, $5p$, $5d$, and $6s$ electrons, the correlation energy difference $\Delta E_{\mathrm{corr}}^{\mathrm{core}}$, the energy difference $\Delta E(n)$ given by MC-DF corrected by BW correlation energies, and experimental $\Delta E(n)$ values.

		Correlation energies (eV)			$\Delta E(n)$ (eV)	
Atom	n	$4f^n5d^16s^2$	$4f^{n+1}5d^06s^2$	$\Delta E_{\mathrm{corr}}^{\mathrm{core}}$	Corrected	Expt.[a]
La	0	−7.730	−9.562	1.832	−0.922	−1.884
Ce	1	−9.962	−10.552	0.590	−0.880	−0.591
Pr	2	−11.107	−11.741	0.635	0.392	0.550
Nd	3	−12.329	−13.559	1.230	0.795	0.839
Pm	4	−13.774	−15.510	1.736	0.985	0.992
Sm	5	−15.753	−17.548	1.795	2.506	2.241
Eu	6	−17.504	−19.140	1.636	3.192	3.453
Gd	7	−19.601	−23.249	3.648	−0.928	−1.357
Tb	8	−23.006	−26.272	3.266	0.242	0.035
Dy	9	−25.513	−28.547	3.034	0.956	0.938
Ho	10	−28.205	−31.437	3.231	0.924	1.039
Er	11	−32.195	−35.970	3.774	0.947	0.890
Tm	12	−36.138	−39.766	3.627	1.518	1.627
Yb	13	−39.733	−42.158	2.425	1.705	2.875

[a] See Ref. [13].

perimental $\Delta E(n)$ values are plotted in Fig. 8. We consider the $5s$ and $5p$ (core) correlation effects obtained from RS calculations. By subtracting the correlation energies given in Table IV from those in Table VI we obtain the correlation energies among the core electrons and those between core and valence electrons. Values range from −7.9 eV for La to −17.9 eV for Yb in the $4f^n5d^16s^2$ configuration, and from −10.4 eV for La to −16.5 eV for Yb in the $4f^{n+1}5d^06s^2$ configuration. These correlation energies are comparable to the $4f$, $5d$, and $6s$ valence correlation energies, showing the importance of intra-core and core-valence correlation effects. In fact, BW gives good results except for La and Yb. The present calculations show the need to include the $5s$ and $5p$ correlation effects.

From Fig. 8 we see that the energy difference $\Delta E(n)$ corrected by RS is slightly inferior to the values corrected by BW. But the RS theory gives the correct n dependence, while BW does not. No general theory of this type therefore exists, and further discussion is required. Higher-order correlation effects might be included, for example.

Although we made two assumptions, (1) and (2) given in the top of this section, and used the second-order perturbation theories; calculated energy differences given in Fig. 8 are close to experiment, showing a validity of the method employed.

IV. CONCLUSION

The energy difference $\Delta E(n)$ given by Eq. (1) has been discussed. The calculational techniques employed were NR-SCF, MC-DF, and the second-order RS and BW perturbation theories. The $\Delta E(n)$ values obtained by MC-DF calculations

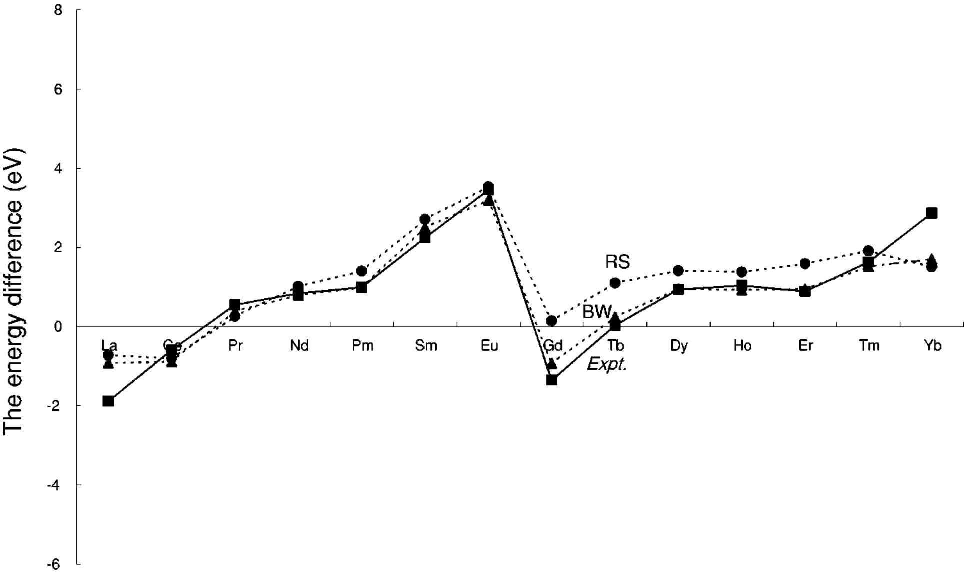

FIG. 8. The energy difference $\Delta E(n)$ given by MC-DF corrected with $\Delta E_{\mathrm{corr}}^{\mathrm{core}}$ obtained by RS and BW calculations and experiment [13]; correlation effects among $5s$, $5p$, $4f$, $5d$, and $6s$ are included.

are lower than the experimental values, while those given by NR-SCF calculations are larger than experiment. By comparing $\Delta E(n)$ obtained by MC-DF and NR-SCF calculations we find that relativistic effects reduce $\Delta E(n)$ by 3–5 eV. On the other hand, $\Delta E(n)$ is increased by valence correlation effects by 0–1.3 eV for the first half of the lanthanide series and 3.0–4.5 eV for the second half. Upon adding valence correlation effects to the $\Delta E(n)$ values given by MC-DF calculation, the resulting values reproduce the experimental $\Delta E(n)$ to within 1 eV except for La. Inclusion of $5s$ and $5p$ core correlation effects further improves $\Delta E(n)$, especially when BW perturbation theory is used. The agreement between the experimental and BW-calculated $\Delta E(n)$ values is almost perfect; the error is less than 0.4 eV, except for La and Yb.

The computer program used in this study was ATOMCI [17] for all of the NR-SCF, RS, and BW perturbation calculations. The GRASP2 package [14] was used for the MC-DF calculations.

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