Benchmark calculations for lanthanide atoms: Calibration of *ab initio* and density-functional methods

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Relativistic *ab initio* pseudopotential and fully relativistic density-functional benchmark calculations have been carried out for the first to fourth ionization potentials as well as the df charge-transfer energies for the whole series of lanthanide atoms. It was found that the two approaches have essentially the same accuracy compared to the experimental values. In addition, it is shown that the present (nonrelativistic) density functionals work fairly well within an otherwise relativistic framework even for the rather compact $4f$ shells, correcting previous statements to the contrary. [S1050-2947(98)02303-8]

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I. INTRODUCTION

The chemistry of lanthanide elements has received much attention in the past three decades [1]. However, the complexity of the open shells of $4f$, $5d$, $6s$, and $6p$ poses a great challenge to theoretical work [2], e.g., the $^{2S+1}L_J$ term of the $4f^n$ subshell may have a spin S as large as 7/2 and an angular momentum L as large as 12. Even more extreme values may result from the coupling of the $4f^n$ subshell to other partially occupied shells of s, p, or d symmetry. Moreover, spin-orbit coupling leads to a large number of energetically adjacent electronic states [3]. Therefore, the knowledge of the energy levels of free lanthanide atoms and ions is far from being complete. However, a detailed knowledge, at least of the low-lying states, is a necessary prerequisite for understanding the behavior of lanthanide atoms in molecules or solids. Theoretical first-principles methods are presently at the edge of successfully dealing with such complicated systems containing lanthanides or actinides [2]. It was found that traditional *ab initio* approaches dealing with relativity at the all-electron Dirac-Coulomb-Breit level and including electron correlation effects by means of coupled-cluster or configuration-interaction (CI) methods need h or even i functions in the one-particle basis sets to yield accurate results [4]. However, such state-of-the-art studies are presently only feasible for atoms by exploiting their spherical symmetry and, to our knowledge, due to its implementation, the method is currently applicable only to some special cases, i.e., closed-shell systems, one or two electrons outside a closed shell, or one or two holes inside a closed shell. In order to be able to treat all lanthanide atoms and also to be able to deal with molecular systems, compromises have to be made with respect to the treatment of relativity and electron correlation. Two such approximate schemes are considered in the present work.

A very successful approach in relativistic quantum chemistry is the *ab initio* pseudopotential method [5], where the

explicit quantum chemical treatment is restricted to the valence electrons and relativistic effects are implicitly accounted for by a proper adjustment of free parameters in the valence model Hamiltonian. Although several sets of such potentials have been published for the lanthanide atoms [6–8], no systematic calibration at the correlated level has been performed for atoms up to now. Another approach, which has gained extensive attention in quantum chemistry during the past decade, is density-functional theory (DFT) [9]. Although in principle the theory based on the works of Hohenberg and Kohn [10] and Kohn and Sham [11] is exact, in practice only approximate approaches are at hand. Since most of the density functionals used nowadays, e.g., the local-density approximation (LDA) and generalized gradient approximation, take the homogeneous electron gas as input and are therefore expected to work well only for slowly varying charge densities, it is reasonable to doubt their good performance for the rather compact $4f$ shells of lanthanide atoms. Indeed, some previous relativistic DFT calculations were not satisfactorily successful in reproducing the term energies of lanthanide atoms, especially when the related states involve occupation changes in the $4f$ shells [12,13]. The present authors recently investigated a number of electronic states of Eu and Yb as well as their cations and found that this failure is, at least partially, an artifact (e.g., basis-set error or use of spherically averaged charge densities) [14,15]. However, in order to establish the reliability of DFT methods for systems containing lanthanides a broader study seems to be needed.

Since both relativistic *ab initio* pseudopotential and density-functional methods will be the methods of choice for the treatment of systems containing heavy elements in the foreseeable future, we decided to investigate their performance for lanthanides in detail. We studied the first to fourth ionization potentials ($V_{i1,2,3,4}$) as well as the $4f^{n+1}6s^2$ -$4f^n5d^16s^2$ excitation energies (df charge-transfer energies) of the whole series of lanthanide atoms (La to Lu). For the *ab initio* calculations we applied the energy-consistent quasirelativistic (QR) pseudopotentials (PPs) of Dolg, Stoll, and Preuß [7], whereas for the density-functional

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calculations the recently developed four-component density-functional program package BDF [14,15] was used. We suggest that the DFT results presented here may serve as a benchmark for other DFT calculations using transformed or simplified relativistic Hamiltonians.

Our paper is organized as follows. In Sec. II we outline the applied *ab initio* pseudopotential and density-functional methods. In Sec. III we present our results and compare them with the available experimental data to display what accuracy the presently available *ab initio* and DFT approaches can actually achieve. Finally, in Sec. IV we give our conclusions.

II. METHODS

A. QR PPs

The method of quasirelativistic energy-consistent *ab initio* pseudopotentials was described in detail elsewhere [6,7] and will be outlined here only briefly. The valence-only model Hamiltonian for an atom or ion with n valence electrons is given as

$$\mathcal{H}_v = -\frac{1}{2}\sum_i^n \Delta_i + \sum_{i<j}^n \frac{1}{r_{ij}} + V_{av} + V_{so}. \tag{1}$$

Here i and j are electron indices. V_{av} denotes a spin-orbit averaged relativistic pseudopotential in a semilocal form

$$V_{av} = -\sum_i \frac{Q}{r_i} + \sum_i \sum_{l,k} A_{lk} \exp(-a_{lk} r_i^2) P_l, \tag{2}$$

where P_l is the projection operator onto the Hilbert subspace of angular momentum l. The spin-orbit term V_{so} may be written as

$$V_{so} = \sum_i \sum_{l>0,k} \frac{2}{2l+1} B_{lk} \exp(-b_{lk} r_i^2) P_l \mathbf{l}_i \mathbf{s}_i P_l. \tag{3}$$

The free parameters A_{lk}, a_{lk}, B_{lk}, and b_{lk} are adjusted to reproduce the valence total energies of a multitude of low-lying electronic states of the neutral atom and its ions. The necessary reference data have been taken from relativistic all-electron calculations. In the present work accurate small-core pseudopotentials for Ce to Yb have been used, e.g., the $1s$ to $3d$ shells were included in the pseudopotential core, while the higher shells were treated explicitly. The orbitals were described by medium-sized one-particle basis sets, e.g., the exponents of a $(12s10p8d8f)$ primitive set were optimized for the lowest state of the $4f^{n+1}6s^2$ configuration of the neutral atom. The contraction coefficients of a $[5s5p4d3f]$ set were derived from atomic natural orbitals (ANOs) of a multireference configuration-interaction ground-state calculation keeping the $4s$, $4p$, and $4d$ shells frozen. The generalized contraction scheme was applied. A $(6g)/[4g]$ ANO correlation set was then derived in the same way starting from the most important exponents of the f set. Finally, two diffuse functions were added in all symmetries up to g, resulting in $(14s12p10d10f8g)/[7s7p6d6f6g]$ basis sets. For the first to fourth ionization potential of all atoms considered here the basis-set errors are less than 0.2 eV

at the Hartree-Fock level. The corresponding pseudopotential errors at the finite-difference level are also typically 0.2 eV or less.

All scalar-relativistic calculations were carried out with the MOLPRO *ab initio* program package [16]. The atomic orbitals were optimized in state-averaged complete active space (CAS) multiconfiguration self-consistent field (SCF) calculations. Dynamic correlation was then accounted for by all single and double excitations from the CASSCF reference in averaged coupled-pair functional (ACPF) calculations [17]. The active space in the CASSCF comprised all open-shell orbitals ($4f$, $5d$, and $6s$), whereas in the ACPF excitations were also allowed from the semicore orbitals ($5s$ and $5p$). No excitations were allowed from the $4s$, $4p$, and $4d$ shells in both CASSCF and ACPF calculations; however, the orbitals were optimized for each state.

Spin-orbit coupling was taken into account by complete configuration-interaction calculations within all open-shell orbitals. The corresponding corrections derived from calculations with and without V_{so} were then added to the scalar-relativistic ACPF results. Since spin-orbit contributions were found to amount to at most a few tenths of an electron volt in the cases considered here, such an additive treatment appears to be justified. Modified versions of the finite-difference programs MCHF [18] and GRASP [19] were used. Due to the use of the state-averaging technique in calculations using MOLPRO and the exploitation of the spherical symmetry in MCHF and GRASP, all *ab initio* results of this work were obtained with eigenfunctions of the appropriate parity and angular-momentum operators.

B. BDF

The BDF program package also has been described elsewhere [14,15]. Briefly, the one-particle Dirac-Kohn-Sham equation (4) based on the Dirac-Coulomb Hamiltonian under the so-called no-pair approximation is solved directly:

$$[c\boldsymbol{\alpha}\cdot\mathbf{p} + (\beta-1)c^2 + V_{ext}(\mathbf{r}) + V_c(\mathbf{r}) + V_{xc}(\rho(\mathbf{r}))]\varphi_j(\mathbf{r})$$
$$= \epsilon_j \varphi_j(\mathbf{r}). \tag{4}$$

Here $\mathbf{p} = -i\boldsymbol{\nabla}$ is the usual momentum operator and c denotes the speed of light, 137.037 a.u. $\boldsymbol{\alpha}$ and β are the Dirac matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \tag{5}$$

where $\boldsymbol{\sigma}$ represents the vector of the 2×2 Pauli spin matrices (σ_x, σ_y, σ_z) and I is the 2×2 unit matrix. The external, Coulomb, and exchange-correlation potentials in Eq. 4 are, respectively,

$$V_{ext}(\mathbf{r}) = -\sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|}, \tag{6}$$

$$V_c(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{7}$$

$$V_{xc}(\rho(\mathbf{r})) = \frac{\delta E_{xc}(\rho(\mathbf{r}))}{\delta \rho}. \qquad (8)$$

The charge density reads

$$\rho(\mathbf{r}) = \sum_{j}^{occ} n_j \varphi_j^\dagger(\mathbf{r}) \varphi_j(\mathbf{r}). \qquad (9)$$

Since relativistic corrections, e.g., the Breit term, to Coulomb and exchange-correlation potentials have only a very limited influence on valence-electron excitation energies of atoms [4,13], they were not considered in the present calculations. Instead, self-interaction corrections (SICs) to the approximate density functionals are significant for the compact shells [13]. The approximate forms for the exchange-correlation potential $V_{xc}(\rho(\mathbf{r}))$ employed in this work are the Perdew-Wang formula [20] within the LDA, a SIC term according to Stoll *et al.* [21], and nonlocal exchange corrections according to Becke [22] as well as nonlocal correlation corrections according to Perdew [23].

The atoms were treated in the same manner as molecules in the calculations by using the double point $D_{\infty h}^*$ group. The jj-coupling scheme was used and Kramer's degeneracy was adopted to carry out moment-polarized calculations for open shells. For the configurations considered here the highest possible moment polarization was always generated. Specifically, the $4f$ shell was occupied as follows: Electrons $1-3$ occupy $4f_{5/2}$ with moment up and electrons $4-7$ occupy $4f_{7/2}$ with moment up; then, electrons $8-10$ occupy $4f_{5/2}$ with moment down and finally electrons $11-14$ occupy $4f_{7/2}$ with moment down. $5d_{3/2}$ and $6s_{1/2}$ were always occupied with moment up when occupied with a single electron. Keeping fixed the highest possible moment polarization, we then used fractional occupation numbers for all moment-polarized subshells with incomplete filling, e.g., for a $4f^1$ configuration each of the three $4f_{5/2,m_j}$ spinors with moment up was occupied by $1/3$ electrons. A final remark appears to be in order here: Although our program works in the jj-coupling scheme, we have to account for the fact that the lanthanides are closer to the nonrelativistic LS-coupling scheme. Therefore, instead of filling first $4f_{5/2}$ and afterward $4f_{7/2}$, we used the prescription given above, which also leads to lower total energies.

The generalized Gauss-Laguerre quadrature [24] and Lebedev quadrature [25] were employed to calculate the radial and angular integrals, respectively. The numerical accuracy of total energies can be further improved to better than 0.01 eV by the generalized transition-state method [26]. The frozen-core approximation, i.e., $[1s^2 - 4d^{10}]$, was employed for all the calculations because relaxation of the $4s$, $4p$, and $4d$ shells did not change the total energies larger than 0.01 eV [15]. Four-component numerical atomic spinors obtained by moment-restricted finite-difference atomic calculations were used for the cores, while the basis sets for the valence orbitals were combinations of the numerical atomic spinors and kinetically balanced double-ζ Slater-type functions (STFs). Such basis sets result in errors less than 0.05 eV.
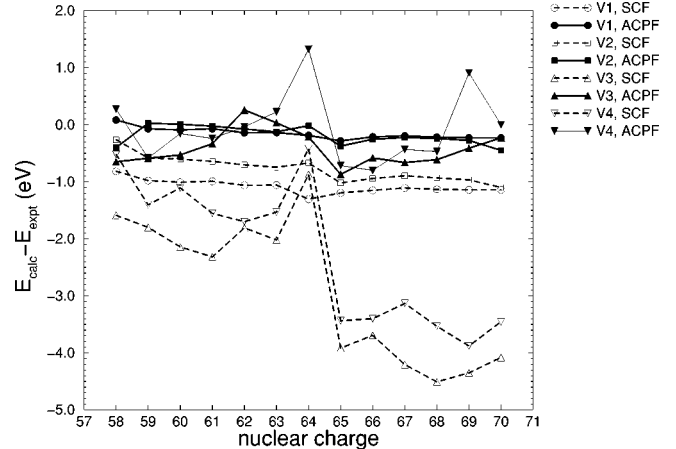

FIG. 1. Absolute errors in the first to fourth ionization potentials from scalar-relativistic *ab initio* pseudopotential calculations without (SCF) and with (ACPF) electron correlation effects. Spin-orbit corrections are not included.

III. RESULTS AND DISCUSSION

Before we discuss our results in detail we want to emphasize that electron correlation effects turn out to be very important (see Fig. 1), e.g., they amount up to about 1 and 4.5 eV for $V_{i1,2}$ and $V_{i3,4}$, respectively. Therefore, uncorrelated Dirac-Hartree-Fock calculations cannot be in quantitative agreement with experiment [27]. Spin-orbit coupling contributions are typically less than 0.2 eV and 0.5 eV for $V_{i1,2}$ and $V_{i3,4}$, respectively, indicating that for many purposes the use of scalar-relativistic Hamiltonians might be sufficiently accurate.

We also want to address a critical point in the DFT studies that is relevant to the fine structure of a multiplet state. The currently existing approximate density functionals lead to unphysical splittings of levels that should be degenerate. These amount to 0.6 eV for the $4f^{13}6s^2$ configuration of the Yb atom [15]. No remedy is currently at hand to avoid this unpleasant feature. However, in a previous study we found that in cases of a fixed $4f$ occupation number these splittings are transferable between different states and therefore energy differences derived for the lowest levels of two states will be only slightly affected by the unphysical splittings due to an error compensation. In cases of a variation of the $4f$ occupation number the error compensation will certainly be less effective, if present at all. In addition to the development of still more accurate density functionals to be used within a single-determinant framework, the extension to multideterminant wave functions might partially cure this defect [28]. Since in the present work we are only interested in the lowest level of a configuration in order to study the general performance of DFT for ionization potentials and excitation energies, we used the average occupation scheme described above.

The calculated ionization potentials $V_{i1} - V_{i4}$ are listed in Tables I–IV, respectively, while the df charge-transfer energies are given in Table V. Some additional results from previous studies are also included. The quality of the present work can be judged from the mean absolute errors (MAEs) given at the bottom of the tables, which were calculated with respect to the experimental values given by Martin *et al.* [3].

TABLE I. First ionization potential (V_{i1} in eV) for the lanthanide atoms from the present fully relativistic density-functional calculations (BDF [14,15]) and *ab initio* quasirelativistic pseudopotential calculations (QR PP) [7] in comparison with other theoretical results [SD, squared Dirac equation with relativistically corrected density functionals (RLDASIC) [13]] and experimental data (Expt. [3]). LDASIC, local-density approximation [20] with self-interaction correction [21]; Becke, nonlocal exchange correction [22]; Perdew, nonlocal correlation correction [23]; BP, both Becke [22] and Perdew [23]; ACPF, averaged coupled-pair functional [17] with spin-orbit coupling corrections. The mean absolute error (MAE) and the largest relative error (LRE) are also given.

Atom	Configurations	BDF				SD	QR PP	
		LDASIC	Becke	Perdew	BP	RLDASIC	ACPF	Expt.
[57]La	$f^0 d^1 s^2 \to f^0 d^2 s^0$	5.59	5.69	5.42	5.51			5.58
[58]Ce	$f^1 d^1 s^2 \to f^1 d^2 s^0$ [a]	5.69	5.75	5.48	5.54	5.8	5.62	5.54
	$f^2 d^0 s^2 \to f^2 d^0 s^1$ [b]	5.21	5.39	5.03	5.21			
[59]Pr	$f^3 d^0 s^2 \to f^3 d^0 s^1$	5.24	5.35	5.06	5.17	5.7	5.39	5.46
[60]Nd	$f^4 d^0 s^2 \to f^4 d^0 s^1$	5.29	5.40	5.09	5.21	5.8	5.44	5.53
[61]Pm	$f^5 d^0 s^2 \to f^5 d^0 s^1$	5.33	5.45	5.13	5.25	5.8	5.48	5.55
[62]Sm	$f^6 d^0 s^2 \to f^6 d^0 s^1$	5.38	5.49	5.17	5.29	5.8	5.51	5.64
[63]Eu	$f^7 d^0 s^2 \to f^7 d^0 s^1$	5.68	5.80	5.45	5.58	5.9	5.53	5.67
		5.42[c]	5.53[c]					
[64]Gd	$f^7 d^1 s^2 \to f^7 d^1 s^1$ [a]	5.84	5.97	5.59	5.72	6.3	6.02	6.15
	$f^8 d^0 s^2 \to f^8 d^0 s^1$ [b]	6.32	6.44	5.88	5.99			
		5.87[c]	5.99[c]					
[65]Tb	$f^9 d^0 s^2 \to f^9 d^0 s^1$	5.65	5.77	5.44	5.56	5.8	5.58	5.86
[66]Dy	$f^{10} d^0 s^2 \to f^{10} d^0 s^1$	5.76	5.88	5.55	5.67	5.8	5.73	5.94
[67]Ho	$f^{11} d^0 s^2 \to f^{11} d^0 s^1$	5.86	5.98	5.66	5.77	5.9	5.82	6.02
[68]Er	$f^{12} d^0 s^2 \to f^{12} d^0 s^1$	5.97	6.08	5.76	5.87	6.0	5.89	6.11
[69]Tm	$f^{13} d^0 s^2 \to f^{13} d^0 s^1$	6.05	6.17	5.84	5.95	6.0	5.95	6.18
[70]Yb	$f^{14} d^0 s^2 \to f^{14} d^0 s^1$ [d]	6.33	6.43	6.11	6.22	6.1	6.02	6.25
		6.06[c]	6.18[c]					
[71]Lu	$f^{14} d^1 s^2 \to f^{14} d^0 s^2$ [e]	5.24	5.30	5.12	5.18	5.7		5.43
	MAE (eV)	0.17	0.11	0.34	0.23	0.2	0.16	
	LRE (%)	5.0	3.8	9.1	7.0	5.0	5.1	

[a]Experimentally measured lowest configurations.

[b]DFT calculated lowest configurations.

[c]DFT FORPT: first-order relativistic perturbation theory [12].

[d]The result of a relativistic all-electron coupled-cluster calculation for Yb with an uncontracted $(31s 26p 21d 15f 10g 6h)$ basis set is 6.34 eV [4].

[e]The result of a relativistic all-electron coupled-cluster calculation for Lu with an uncontracted $(34s 25p 20d 15f 10g 6h)$ basis set is 5.30 eV [4].

Two points have to be taken into account. First, the *ab initio* and DFT MAEs refer to the atoms Ce to Yb and La to Lu, respectively, i.e., they are not defined for the same set of systems. Second, some experimental data are not available, e.g., for Pm, and some other values bear large error bars [3]. Nevertheless, we think that the MAEs given in Tables I–V still allow us to roughly judge the performance of the *ab initio* and DFT approaches presented here.

It can be seen from Tables I and II that both methods presented here reproduce V_{i1} and V_{i2} fairly well, i.e., the MAEs are below 0.20 eV for the *ab initio* and BDF (LDASIC) results. Nonlocal corrections [Becke [22], Perdew [23], or Becke-Perdew (BP)] do not change the LDASIC results significantly. DFT calculations of Forstreuter *et al.* [13] based on the squared Dirac Hamiltonian (SD) using both relativistically [29] and SIC [30] corrected local-density functionals (RLDASIC) yielded V_{i1} of similar quality to our DFT results. Nevertheless, it is also discernable that the dif-

ferences for V_{i1} between the BDF (LDASIC) and SD (RLDASIC) results amount to 0.5 eV for lighter elements, although they are in good agreement for heavier elements. However, the BDF results show more systematic errors when compared to experiment. They are also closer to other DFT results taking relativity into account as a first-order perturbation [12] as well as fully relativistic coupled-cluster calculations [4] (cf. Table I). The MAE for V_{i2} by SD (RLDASIC) [13] amounts to 0.50 eV, i.e., it is a factor of 2 larger than the present values.

We mention that in contrast to the *ab initio* method, both BDF (cf. Tables I and II) and SD (RLDASIC) [31] calculations do not reproduce the experimental ground states for Ce/Ce$^+$ and Gd/Gd$^+$. This might be attributed to the fact that nondynamic correlation effects due to near-degenerate configurations are missing within the single-determinant formulation of DFT. A combination of multireference wave

TABLE II. Second ionization potential (V_{i2} in eV). For other explanations see Table I.

Atom	Configurations	BDF				SD	QR PP	
		LDASIC	Becke	Perdew	BP	RLDASIC	ACPF	Expt.
[57]La	$f^0d^2s^0 \rightarrow f^0d^1s^0$	10.85	10.93	10.74	10.81			211.06
[58]Ce	$f^1d^2s^0 \rightarrow f^2d^0s^0$ [a]	9.54	9.65	9.50	9.61	8.8	11.06	10.85
	$f^2d^0s^1 \rightarrow f^2d^0s^0$ [b]	10.43	10.49	10.26	10.32			
[59]Pr	$f^3d^0s^1 \rightarrow f^3d^0s^0$	10.61	10.68	10.44	10.51	10.9	10.57	10.55
[60]Nd	$f^4d^0s^1 \rightarrow f^4d^0s^0$	10.79	10.86	10.62	10.68	11.0	10.73	10.73
[61]Pm	$f^5d^0s^1 \rightarrow f^5d^0s^0$	10.95	11.02	10.77	10.84	11.3	10.87	10.90
[62]Sm	$f^6d^0s^1 \rightarrow f^6d^0s^0$	11.11	11.17	10.93	10.99	11.5	10.98	11.07
[63]Eu	$f^7d^0s^1 \rightarrow f^7d^0s^0$	11.27	11.35	11.10	11.19	11.6	11.11	11.24
[64]Gd	$f^7d^1s^1 \rightarrow f^7d^1s^0$ [a]	12.26	12.30	12.13	12.17	12.7	12.05	12.09
	$f^8d^0s^1 \rightarrow f^8d^0s^0$ [b]	11.40	11.47	11.20	11.27			
[65]Tb	$f^9d^0s^1 \rightarrow f^9d^0s^0$	11.54	11.61	11.33	11.41	11.9	11.14	11.52
[66]Dy	$f^{10}d^0s^1 \rightarrow f^{10}d^0s^0$	11.67	11.75	11.46	11.54	12.1	11.41	11.67
[67]Ho	$f^{11}d^0s^1 \rightarrow f^{11}d^0s^0$	11.80	11.88	11.58	11.66	12.2	11.57	11.80
[68]Er	$f^{12}d^0s^1 \rightarrow f^{12}d^0s^0$	11.93	12.01	11.70	11.79	12.3	11.69	11.93
[69]Tm	$f^{13}d^0s^1 \rightarrow f^{13}d^0s^0$	12.19	12.28	11.96	12.05	12.5	11.77	12.05
[70]Yb	$f^{14}d^0s^1 \rightarrow f^{14}d^0s^0$ [c]	12.13	12.23	11.90	12.00	12.6	11.73	12.18
[71]Lu	$f^{14}d^0s^2 \rightarrow f^{14}d^0s^1$ [d]	13.86	13.97	13.60	13.71	14.2		13.90
	MAE (eV)	0.15	0.19	0.26	0.18	0.5	0.18	
	LRE (%)	1.4	1.9	2.9	2.3	5.1	3.8	

[a]Experimentally measured lowest configurations.
[b]DFT calculated lowest configurations.
[c]The result of a relativistic all-electron coupled-cluster calculation for Yb with an uncontracted ($31s26p21d15f10g6h$) basis set is 12.14 eV [4].
[d]The result of a relativistic all-electron coupled-cluster calculation for Lu with an uncontracted ($34s25p20d15f10g6h$) basis set is 14.12 eV [4].

TABLE III. Third ionization potential (V_{i3} in eV). For other explanations see Table I.

Atom	Configurations	BDF				SD	QR-PP	
		LDASIC	Becke	Perdew	BP	RLDASIC	ACPF	Expt.
[57]La	$f^0d^1s^0 \rightarrow f^0d^0s^0$	18.74	18.87	18.54	18.67			19.18
[58]Ce	$f^2d^0s^0 \rightarrow f^1d^0s^0$	20.53	20.61	20.26	20.34	22.6	19.36	20.20
[59]Pr	$f^3d^0s^0 \rightarrow f^2d^0s^0$	21.79	21.87	21.53	21.61	23.9	21.04	21.62
[60]Nd	$f^4d^0s^0 \rightarrow f^3d^0s^0$	22.44	22.53	22.19	22.28	24.9	21.52	22.1±0.3
[61]Pm	$f^5d^0s^0 \rightarrow f^4d^0s^0$	23.39	23.48	23.15	23.23	25.7	21.87	22.3±0.4
[62]Sm	$f^6d^0s^0 \rightarrow f^5d^0s^0$	24.22	24.31	23.98	24.07	26.6	23.14	23.4±0.3
[63]Eu	$f^7d^0s^0 \rightarrow f^6d^0s^0$	24.64	24.72	24.41	24.46	27.3	24.56	24.92
[64]Gd	$f^7d^1s^0 \rightarrow f^7d^0s^0$	20.13	20.19	19.92	19.98	20.9	20.59	20.63
[65]Tb	$f^9d^0s^0 \rightarrow f^8d^0s^0$	22.75	22.79	22.37	22.41	23.7	21.19	21.91
[66]Dy	$f^{10}d^0s^0 \rightarrow f^9d^0s^0$	23.62	23.66	23.25	23.30	24.3	22.25	22.8±0.3
[67]Ho	$f^{11}d^0s^0 \rightarrow f^{10}d^0s^0$	23.36	23.42	23.01	23.07	25.1	22.04	22.84
[68]Er	$f^{12}d^0s^0 \rightarrow f^{11}d^0s^0$	24.03	24.10	23.69	23.75	25.6	21.88	22.74
[69]Tm	$f^{13}d^0s^0 \rightarrow f^{12}d^0s^0$	24.53	24.61	24.21	24.30	25.9	22.89	23.68
[70]Yb	$f^{14}d^0s^0 \rightarrow f^{13}d^0s^0$	25.03	25.10	24.70	24.76	26.3	24.27	25.05
[71]Lu	$f^{14}d^0s^1 \rightarrow f^{14}d^0s^0$ [a]	21.01	21.10	20.70	20.79	21.5		20.96
	MAE (eV)	0.56	0.60	0.45	0.46	2.1	0.58	
	LRE (%)	5.7	6.0	4.2	4.4	15.3	4.3	

[a]The result of a relativistic all-electron coupled-cluster calculation for Lu with an uncontracted ($34s25p20d15f10g6h$) basis set is 20.97 eV [4].

TABLE IV. Fourth ionization potential (V_{i4} in eV). For other explanations see Table I.

Atom	Configurations	BDF				QR PP	
		LDASIC	Becke	Perdew	BP	ACPF	Expt.
^{57}La	$5s^25p^6\rightarrow5s^25p^5$	49.18	49.31	48.94	49.07		49.95
^{58}Ce	$f^1d^0s^0\rightarrow f^0d^0s^0$	37.54	37.62	37.22	37.30	36.05	36.76
^{59}Pr	$f^2d^0s^0\rightarrow f^1d^0s^0$ [a]	39.10	39.19	38.80	38.88	38.48	38.98
^{60}Nd	$f^3d^0s^0\rightarrow f^2d^0s^0$	40.50	40.59	40.20	40.30	40.26	40.4±0.1
^{61}Pm	$f^4d^0s^0\rightarrow f^3d^0s^0$	41.19	41.29	40.91	41.01	40.81	41.1±0.6
^{62}Sm	$f^5d^0s^0\rightarrow f^4d^0s^0$	42.31	42.41	42.04	42.14	41.26	41.4±0.7
^{63}Eu	$f^6d^0s^0\rightarrow f^5d^0s^0$	43.34	43.43	43.07	43.17	42.73	42.7±0.6
^{64}Gd	$f^7d^0s^0\rightarrow f^6d^0s^0$	44.26	44.36	44.00	44.10	44.86	44.0±0.7
^{65}Tb	$f^8d^0s^0\rightarrow f^7d^0s^0$	40.89	40.92	40.47	40.59	38.96	39.37
^{66}Dy	$f^9d^0s^0\rightarrow f^8d^0s^0$	42.03	42.07	41.63	41.67	40.79	41.4±0.4
^{67}Ho	$f^{10}d^0s^0\rightarrow f^9d^0s^0$	43.08	43.13	42.69	42.74	42.10	42.5±0.6
^{68}Er	$f^{11}d^0s^0\rightarrow f^{10}d^0s^0$	42.81	42.87	42.43	42.50	42.06	42.7±0.4
^{69}Tm	$f^{12}d^0s^0\rightarrow f^{11}d^0s^0$	43.58	43.66	43.23	43.31	43.32	42.7±0.4
^{70}Yb	$f^{13}d^0s^0\rightarrow f^{12}d^0s^0$	44.40	44.48	44.05	44.12	43.11	43.56
^{71}Lu	$f^{14}d^0s^0\rightarrow f^{13}d^0s^0$	45.10	45.17	44.75	44.83		45.25
	MAE (eV)	0.56	0.61	0.42	0.43	0.45	
	LRE (%)	3.9	3.9	2.8	2.9	2.0	

[a]The result of a relativistic all-electron coupled-cluster calculation for Pr with an uncontracted $(29s23p19d14f10g6h4i)$ basis set is 38.61 eV [4].

functions with DFT might be able to improve the results [28].

The rather good performance of both *ab initio* and DFT approaches for V_{i1} and V_{i2} is mainly related to the fact that for almost all atoms (an exception is Ce) the $4f$ occupation remains unchanged. Harder tests are the third and fourth ionization potentials where the $4f$ occupation is changed by one or two electrons. For V_{i3} the MAE of the *ab initio* data is

TABLE V. df charge-transfer energies (eV) defined as $\Delta_{df} = E(f^nd^1s^2)-E(f^{n+1}d^0s^2)(n=0-13$ for La to Yb). Density-functional results are for an averaged occupation of the open shells. For other explanations see Table I.

Atom	BDF				QR PP	
	LDASIC	Becke	Perdew	BP	ACPF	Expt.
^{57}La	−1.34	−1.32	−1.52	−1.49		−1.88
^{58}Ce	0.40	0.46	0.31	0.36	−0.96	−0.59
^{59}Pr	1.33	1.34	1.25	1.26		0.55
^{60}Nd	1.77	1.86	1.69	1.78		0.84
^{61}Pm	2.49	2.52	2.43	2.46		
^{62}Sm	3.13	3.16	3.07	3.10		2.24
^{63}Eu	3.74	3.78	3.68	3.72		3.33[a]
^{64}Gd	0.47	0.45	0.27	0.25	−2.22	−1.36
^{65}Tb	1.40	1.39	1.22	1.22	−0.15	0.04
^{66}Dy	2.23	2.23	2.07	2.07	0.60	0.94
^{67}Ho	1.82	1.83	1.69	1.69	0.65	1.04
^{68}Er	2.43	2.44	2.31	2.32	0.36	0.89
^{69}Tm	2.99	3.00	2.89	2.90	1.30	1.63
^{70}Yb	3.46	3.50	3.36	3.40		2.88
MAE (eV)	1.02	1.04	0.90	0.93	0.43	

[a]Estimated value [33].

0.58 eV, whereas the ones for the BDF results range from 0.45 eV to 0.60 eV at different levels of calculations. A much larger MAE of 2.1 eV as well as larger fluctuations of 1–4 eV in the absolute deviations are found for the SD (RLDASIC) data [13]. Since in the framework of density-functional calculations the squared Dirac Hamiltonian used by these authors should be completely equivalent to the Dirac Hamiltonian used in our work, the differences have to be traced to other sources, except for the small differences between the different density functionals used in these two calculations. It has been found that roughly half of the error stems from the sole use of an incomplete STF basis set [31], whereas a combination of numerical functions and STFs was used in the present work. In addition, Forstreuter *et al.* [13] used spherically averaged charge densities in contrast to the present polarized ones. For the fourth ionization potential the MAE is 0.45 eV for the *ab initio* results and ranges from 0.42 eV to 0.61 eV for the BDF values. Of course, one has to keep in mind that the error bars in the experimental results amount to 0.7 eV (cf. Table IV).

Another less robust criterion than the MAE to judge the quality of the calculations is the largest relative error, which is relevant to the amplitude of the fluctuations of the calculated results with respect to the experimental values. From Tables I–IV one can see that the largest relative errors are typically about 2–6 % for all the approaches included here, with an exception of 15.3% in the SD (RLDASIC) V_{i3} results [13].

It is worthwhile to mention that the present BDF results for Yb, Lu, and Pr are very close to those obtained by the fully relativistic all-electron coupled-cluster calculations using very large uncontracted basis sets (cf. the footnotes in Tables I–IV), whereas the present approach is computationally much cheaper.

A real challenge for computational methods appears to be the calculation of $4f^{n+1}6s^2$-$4f^n5d^16s^2$ excitation energies (df charge-transfer energies). *Ab initio* results for $4f^n5d^16s^2$ are quite difficult to get due to the too large active space resulting from open d and f shells. Moreover, for Sm, Eu, and Yb some states of $4f^{n+1}6s^16p^1$ are lower in energy than the lowest solutions for $4f^n5d^16s^2$ and cause root flipping problems in the CI. Convergence also could not be achieved for Pr, Nd, and Pm where $4f^n5d^26s^1$ is nearly degenerate. In fact, we were only able to perform the calculations for Ce and Gd with a complete active space: The errors in the excitation energies after correction for spin-orbit coupling are 0.37 eV and 0.86 eV, respectively. In both cases the configuration with the larger $4f$ occupation number is too high in energy, most likely reflecting the incomplete correlation treatment due to the neglect of higher than g functions in the basis sets. In order to obtain results for the atoms Tb to Tm the occupation of the $5d$ orbitals in the active space had to be restricted to one in the reference wave function. Compared to the lowest experimental levels, the MAEs of the BDF results range from 0.90 eV to 1.04 eV, whereas 0.43 eV is obtained at the *ab initio* level. The DFT calculations systematically overestimate the excitation energies and the *ab initio* calculations underestimate them. We mention that the MAE of nonrelativistic calculations is more than 2 eV [32]. Again, the remaining large deviations of relativistic DFT calculations might be accounted for by the missing nondynamic correlation effects, which are expected to be larger for the df charge-transfer energies than for the ionization potentials because occupation changes occur to both f and d shells.

IV. CONCLUSIONS

Benchmark calculations using both *ab initio* and DFT approaches have been performed for the whole series of lanthanide atoms. The results show that both approaches have essentially the same accuracy when compared to experimental data. Clearly, the current *ab initio* results might be systematically improved as soon as this is feasible from a computational point of view, e.g., by including higher-order angular-momentum basis functions. The presently available approximate (nonrelativistic) density functionals work fairly well in an otherwise relativistic framework for the rather compact $4f$ shells, correcting previous opposite statements by other authors. Moreover, a combination of multireference wave functions with DFT might even be able to further improve the performance of DFT in the open-shell systems studied here. Work along this line is under way in our laboratory.

V. ACKNOWLEDGMENTS

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