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The Beijing four-component density functional program package (BDF) and its application to EuO, EuS, YbO and YbS

Wenjian Liu[1,2], **Gongyi Hong**[1], **Dadi Dai**[1], **Lemin Li**[1], **Michael Dolg**[2]

[1] State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China
[2] Max-Planck-Institut für Physik komplexer Systeme, Bayreuther Strasse 40, D-01187 Dresden, Germany

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Abstract. A four-component density functional program package (Beijing Density Functional), suitable for the calculation of total-energy-related chemical properties of systems containing heavy atoms, was developed. The code is based on modern sophisticated exchange-correlation functionals and was applied to calculate the spectroscopic constants of the lanthanide diatomic molecules of EuO, EuS, YbO and YbS. It is suggested that the *experimental* bond lengths for EuS and YbS, derived from empirical interpolations, need to be revised. Relativistic effects on the electronic structure are discussed and compared with results from previous work. The involvement of the lanthanide valence orbitals in chemical bonding is investigated with a newly developed population and bonding analysis approach.

Key words: Relativistic effects – Density functional theory – Beijing Density Functional – Lanthanide diatomics – Atomic orbitals in molecules

1 Introduction

Over the past decades the chemistry of lanthanides has been attractive and challenging to both experimentalists and theoreticians [1–4]. On the one hand, well-assigned experimental data are available for only a few, mostly diatomic, lanthanide compounds [5–8]. On the other hand, theoretical calculations are rather complicated due to the complex electronic structure and large electron correlation effects arising from the open 4*f*, 5*d*, 6*s* and 6*p* valence shells as well as significant relativistic effects due to the heavy nuclei (Z = 57 for La to Z = 71 for Lu) [9]. Nevertheless, various theoretical investigations have been performed [9, 10]. First of all, semi-empirical approaches such as ligand field theory [11, 12], relativistic extended Hückel theory [13] and INDO methods [14–17] have been shown to be very useful in interpreting many geometric, spectroscopic and magnetic properties of lanthanide compounds. Ab initio energy-consistent quasirelativistic pseudopotentials (QR-PP) have been designed and applied to predict low-lying electronic states of lanthanide systems [18–22]. Similar shape-consistent pseudopotentials are also available and have been used in several applications [23]. Finally, density functional theory (DFT) has played an important role in explaining the electronic structure and chemical bonding of lanthanide compounds [9, 10, 24–27]. Recently the Amsterdam density functional program package (AMOL) [28], in which relativity was accounted for as a first-order perturbation, was used to derive the spectroscopic constants of some lanthanide diatomics [29, 30].

The goal of the present work is threefold. First, since the computational effort necessary to carry out pure ab initio calculations that account well for both relativistic effects and electron correlation effects is tremendous, it is worthwhile to develop a four-component fully relativistic density functional program package which can deal with total-energy-related chemical properties accurately, but at a much smaller expense compared to standard quantum chemical methods. Such a program package, the Beijing density functional (BDF), is presented in Sect. 2. Second, modern density functional theory has been shown to perform well for light element systems as well as transition metal complexes [31], but yields less satisfactory results for inner 4*f* shells [29]. The work presented in Sect. 3.1 shows, however, that the currently available (nonrelativistic) functionals can also work reasonably well in these cases when a fully relativistic framework is applied. Third, the amount of the participation of Ln 4*f* orbitals in chemical bonding has been discussed controversially for a long time. Some authors argued that 4*f* orbitals are significant for chemical bonding [24], whereas others claimed that 4*f* orbitals are

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Correspondence to: W. Liu, Max-Planck-Institut für Physik komplexer Systeme, Bayreuther Strasse 40, D-01187 Dresden, Germany (e-mail: lwj@idefix.mpipks-dresden.mpg.de)

essentially core-like and thus have no significant (direct) contributions to chemical bonding [14]. A well-defined method, atomic orbitals in molecules (AOIM) [32], with the merit of basis set independence and characterized by a clear physical picture also in the case of calculations with extended basis sets, will be employed in Sect. 3.2 to analyze the chemical bonding of the diatomic lanthanide molecules studied here.

Experimental evidence (cf. [7, 8]) indicates that the ground states of the lanthanide monoxides arise from $4f^{n}\sigma^{1}$ superconfigurations ($\omega_e \approx 830$ cm^{-1}), except in the case of EuO and YbO where $4f^{n+1}$ superconfigurations ($\omega_e \approx 670$ cm^{-1}) are preferred due to the enhanced stability of a half-filled or filled $4f$ shell, respectively. EuS and YbS are suspected to have a similar electronic structure. DFT [29] calculations confirmed the above point of view. Ab initio QR-PP calculations [19, 21], however, predicted that in YbO $4f^{13}\sigma^{1}(^3\Sigma^+(0^-))$ is lower than $4f^{14}(^1\Sigma^+(0^+))$. In this contribution we will only focus on the $4f^{n+1}$ superconfigurations. The question whether the $^1\Sigma^+(0^+)$ or $^3\Sigma^+(0^-)$ state is the real ground state for YbO will be investigated in detail elsewhere. The present calculations will be compared with other theoretical results and available experimental data.

2 Theoretical methods

The Hohenberg-Kohn theorem [33], underlying density functional theory, has also been shown to be valid for the relativistic case [34]. The corresponding Dirac-Kohn-Sham equations have been formulated by Rajagopal [35] and MacDonald and Vosko [36]. An overview, including the quantum electrodynamical basis, of relativistic density functional theory has been given by Gross and Dreizler [37] and Engel et al. [38].

Within the so-called no-sea approximation the Dirac-Kohn-Sham equation for a spinor φ_j reads

$$(c\vec{\alpha}\cdot\vec{p} + (\beta - 1)c^2 + V^{DKS}(\vec{r}))\varphi_j(\vec{r}) = \epsilon_j\varphi_j(\vec{r}). \tag{1}$$

Here $\vec{p} = -i\vec{\nabla}$ is the usual momentum operator and c denotes the speed of light. $\vec{\alpha}$ and β are the Dirac matrices

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \tag{2}$$

where $\vec{\sigma}$ 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 potential operator reads

$$V^{DKS}(\vec{r}) = V_{ext}(\vec{r}) + V_c(\vec{r})\phi_c^R + V_{xc}(\rho(\vec{r}))\phi_{xc}^R \tag{3}$$

where ϕ_c^R and ϕ_{xc}^R are relativistic corrections, e.g., the Breit term to the Coulomb and exchange-correlation potentials, respectively. In fact, it has been shown that these corrections are significant only for the innermost shells of heavy atoms and turn out to be negligible for valence shells [38, 39]. In heavy-atom-containing molecular calculations the frozen-core approximation usually has to be adopted, which means that the errors due to the neglect of these relativistic corrections are kept constant along the whole energy surface. On the other hand, the available relativistic corrected exchange-correlation functionals are still not fully satisfactory [38]. Neglecting the relativistic corrections to the electron-electron interaction ($\phi_c^R = 1$, $\phi_{xc}^R = 1$) the three terms in Eq. (3) read

$$V_{ext}(\vec{r}) = -\sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|}, \tag{4}$$

$$V_c(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2, \tag{5}$$

$$V_{xc}(\rho(\vec{r})) = \frac{\delta E_{xc}(\rho(\vec{r}))}{\delta\rho}. \tag{6}$$

The charge density is given as

$$\rho(\vec{r}) = \sum_j n_j \varphi_j^+(\vec{r})\varphi_j(\vec{r}). \tag{7}$$

Although the exact form of the exchange-correlation potential $V_{xc}(\rho(\vec{r}))$ remains unknown, some sophisticated (nonrelativistic) functionals are available, e.g., the Vosko-Wilk-Nusair formula [40] within the local density approximation (LDA), a self-interaction (SI) correction according to Stoll et al. [41] and nonlocal exchange corrections (NLx) according to Becke [42] as well as nonlocal correlation corrections (NLc) according to Perdew [43] and Lee et al. [44]. All these functionals were implemented in the BDF. The Dirac-Slater discrete variational method to solve the Dirac-Kohn-Sham Eq. (1) developed by Ellis and coworkers [45, 46] was the first available four-component density functional program package. The multi-dimensional Diophantine numerical integration and self-consistent multipolar (SCM) fitting of the charge density were employed to calculate the matrix elements [45]. This scheme works for orbital-related properties such as photoelectron or optical spectra as well as orbital contributions to chemical bonding [46] but precludes calculations of potential energy curves. An old version of this program served as a starting point for the BDF code.

The strategy to improve the accuracy of molecular total energy calculations has been discussed in detail elsewhere [47]. Briefly, the partition functions of Becke [48] were employed to decompose the multicenter molecular integrals into a summation over one-center contributions. The one-center radial integrals can be accurately calculated by the generalized Gauss-Laguerre quadrature [49], while the angular integrals can be performed by the Lebedev quadrature [50]. To solve Poisson's equations efficiently the charge density [Eq. (7)] can be expanded into a rapidly convergent multipolar form [51], namely

$$\rho_{model}(\vec{r}) = \sum_A \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} Y_{lm}(\widehat{\vec{r},\vec{R}_A})\rho_{Alm}(|\vec{r} - \vec{R}_A|), \tag{8}$$

$$\rho_{Alm}(|\vec{r} - \vec{R}_A|) = \int Y_{lm}(\widehat{\vec{r},\vec{R}_A})P_A(\vec{r})\rho(\vec{r})d\Omega, \tag{9}$$

in which $P_A(\vec{r})$ is the partition function centered on atom A according to Becke's formula [48]. The corresponding Coulombic potential has the form

$$V(\vec{r}) = \sum_A \sum_{l=0}^{l'_{max}} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} Y_{lm}(\widehat{\vec{r}, \vec{R}_A}) V_{Alm}(|\vec{r} - \vec{R}_A|), \quad (10)$$

$$V_{Alm}(r_A) = r_A^{-l-1} \int_0^{r_A} \rho_{Alm}(s) s^{l+2} ds + r_A^l \int_{r_A}^{\infty} \rho_{Alm}(s) s^{1-l} ds. \quad (11)$$

The l_{max} in Eq. (8) and l'_{max} in Eq. (10) were chosen to be 5 in the present calculations. The above scheme combines the merits of the best currently available numerical techniques in DFT calculations and was shown to perform very efficiently [47, 52].

The described numerical calculation of the necessary matrix elements allows the use of any type of basis functions. In this work the frozen-core approximation was employed for the following cores: $[1s^2 - 4d^{10}]$ for europium and ytterbium, $[1s^2]$ for oxygen and $[1s^2 - 2p^6]$ for sulfur. Four-component numerical atomic orbitals obtained by finite-difference atomic calculations were used for the cores, while the basis sets for the valence orbitals were the combination of the numerical atomic orbitals and kinetically balanced double-zeta, Slater-type functions. The diffuse $2p$ ($3p$) functions, two sets of polarized $3d$ functions and one set of $4f$ functions were added to oxygen (sulfur).

Finally, the generalized transition-state method developed by Ziegler and Rauk [53] was adapted to the frozen-core approximation and the nonlocal corrections to improve the numerical accuracy of the total energies and to obtain the dissociation energies directly [47]. This scheme essentially treats the reference atoms and molecular states in a counterpoise way and can avoid the numerical errors due to the subtraction of two large total energies. The resultant basis set superposition error is about 0.1 eV and the dissociation energy was found to be convergent to 0.001 eV with respect to the number of integration points. Since the emphasis of the current work was on the numerical accuracy rather than on the speed of the computations, we used a comparatively large number of integration points: the number of radial × angular grid points was 100 × 194 and 80 × 194 for the lanthanide and chalcogen atoms, respectively.

3 Results and discussion

3.1 Atomic calculations

The term energies for several electronic states of the europium and ytterbium atoms and their cations, which

Table 1. Atomic energies (in eV) from the present fully relativistic density functional calculations (BDF) in comparison to experimental data (Expt. [55]) and results from other theoretical methods (AMOL [29]; *P-PP* scalar quasirelativistic pseudopotential [18]; *ACPF* averaged coupled pair functional [54]); *LDASI* local density approximation [40] with self-interaction correction [41]; *NLx* nonlocal exchange correction [42]; *NLc* nonlocal correlation correction [43]; *NLxc* both nonlocal exchange and correlation corrections [42, 43]. Nonrelativistic values are given in square brackets. Spin-orbit averaged experimental values are given in parentheses

Atom	Configuration[a]	Term	BDF				AMOL		PP		
			LDASI	NLx	NLc	NLxc	LDASI	NLx	Expt.	ACPF	(Expt.)
Eu	f^7s^2	$^8S_{7/2}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	(0.00)
Eu	$f^7s^1d^1$	$^{10}D_{5/2}$	1.37	1.46	1.23	1.31	1.49	1.50	1.60	1.73	(1.66)
			[0.84]	[0.93]	[0.72]	[0.81]	[0.84]	[0.93]			
Eu	$f^7s^1p^1$	$^{10}P_{7/2}$	1.82	1.87	1.66	1.70			1.74	2.38	(1.84)
Eu	$f^6s^2d^1$	^8H	3.74	3.78	3.68	3.72	4.74	4.84			(3.67)[b]
Eu^+	f^7s^1	$^9S_4$	5.68	5.80	5.45	5.58	5.42	5.53	5.67	5.50	(5.67)
Eu^+	f^6s^2	$^7F_0$	10.00	10.09	9.86	9.95					
Eu^+	$f^6s^1d^1$	^9H	9.75	9.90	9.45	9.60	10.57	10.79		9.77	(9.90)[b]
Eu^{++}	f^7s^0	$^8S_{7/2}$	16.95	17.15	16.55	16.77			16.91	16.64	(16.91)
Eu^{++}	f^6s^1	$^8F_{1/2}$	22.51	22.71	22.13	22.33			22.63	22.29	(22.99)
Eu^{++}	f^6s^1	$^6F_{1/2}$	22.83	23.03	22.49	22.68			22.89		(23.26)
Eu^{+++}	f^6s^0	$^7F_0$	41.59	41.87	40.96	41.23			41.83	41.28	(42.22)
Yb	$f^{14}s^2$	$^1S_0$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	(0.00)
Yb	$f^{14}s^1p^1$	$^3P_0$	2.38	2.40	2.23	2.25	2.43	2.46	2.14	3.06	(2.34)
Yb	$f^{14}s^1d^1$	$^3D_1$	2.84	2.90	2.73	2.78	2.78	2.85	3.04	3.50	(3.09)
			[2.00]	[2.08]	[1.90]	[1.99]	[1.97]	[2.05]			
Yb^+	$f^{14}s^1$	$^2S_{1/2}$	6.33	6.43	6.11	6.22			6.25	5.99	(6.25)
Yb^+	$f^{13}s^2$	$^2F_{7/2}$	9.02	9.09	8.80	8.88	9.61	9.70	8.91	9.13	(9.43)
Yb^{++}	$f^{14}s^0$	$^1S_0$	18.45	18.66	18.01	18.22			18.44	17.80	(18.44)
Yb^{++}	$f^{13}s^1$	$^3F_4$ [c]	22.80	23.00	22.34	22.53	23.33	23.53	22.74	22.58	
											(23.30)
Yb^{++}	$f^{13}s^1$	$^1F_3$ [d]	22.85	23.04	22.39	22.58			22.78		
Yb^{+++}	$f^{13}s_0$	$^2F_{7/2}$	43.48	43.76	42.71	42.98			43.49	42.63	(44.03)

[a] The jj coupling sheme was used in present calculations, e.g., the f^6 configuration corresponds to $f^3_{5/2} f^3_{7/2}$, whereas p^1 and d^1 correspond to $p^1_{1/2}$ and $d^1_{3/2}$, respectively. The non-half-filled open shells were calculated with averaged fractional occupation. Kramer's degeneracy was adoped to perform the moment polarization calculations in the same way as in nonrelativistic spin polarization calculations

[b] The H-states have not been measured. The spin-orbit averaged energies were estimated by Wang et al. [29]

[c,d] The experimental labels $(j_1, j_2)_J$ are $(7/2, 1/2)_4$ and $(7/2, 1/2)_3$, respectively

were calculated in the same manner as the molecules, are listed in Table 1. The jj coupling scheme was employed and Kramer's degeneracy was adopted to carry out moment polarization calculations for open shells in the same way as in nonrelativistic spin polarization calculations [46]. Self-consistent field (SCF) calculations were performed within the local density approximation with self-interaction correction (LDASI) [40, 41]. NLx corrections [41] and NLc corrections [43] or both of them (NLxc) were added as perturbations for the converged charge density. The double point $D^*_{8\mathrm{h}}$ group was employed in the calculations. The non-half-filled open shells, e.g., $f^7_{7/2}$ for the Yb$^+$ $f^{13}s^2$ configuration, were calculated with averaged fractional occupation in order to obey the Aufbauprinzip. We also performed the calculations on the states with electronic holes in the individual $(\mathrm{j}, \mathrm{m_j})$ sublevels. Again, take Yb$^+$ $f^{13}s^2$ as an example: the obtained term energies at the LDASI level are 9.32 eV for one hole in $(7/2, 1/2)$, 9.07 eV for one hole in $(7/2, 3/2)$, 9.05 eV for one hole in $(7/2, 5/2)$, and 9.62 eV for one hole in $(7/2, 7/2)$, respectively.

The differences between these numbers are due to symmetry breaking occurring in $D^*_{8\mathrm{h}}$. The Aufbauprinzip was disobeyed in these calculations, i.e., the unoccupied f spinor is lower in energy than some occupied ones; thus the configuration with averaged fractional occupation can give a lower-term energy, i.e., 9.02 eV, which has to be compared with the lowest experimental value of 8.91 eV. Other theoretical results [21, 29, 54] obtained in the LS coupling scheme and available experimental data [55] are also given in Table 1 for comparison. The experimental values for the ^8H state of Eu($f^6s^2d^1$) and the ^9H state of Eu$^+$($f^6s^1d^1$) are not available, but were estimated by Wang et al. [29].

It can be seen from Table 1 that the maximum absolute deviations of the current relativistic calculations from available experimental data are typically less than 0.5 eV at all the levels of calculations, whereas nonrelativistic calculations fail to reproduce the experimental values. The standard deviations from available experimental values for europium are 0.14 eV (LDASI), 0.14 eV (NLx), 0.46 eV (NLc) and 0.29 eV (NLxc). The corresponding values for ytterbium are 0.13 eV (LDASI), 0.24 eV (NLx), 0.42 eV (NLc) and 0.25 eV (NLxc). Obviously, relativistic LDASI performs very well for all the states studied here. NLx and NLc corrections tend to increase and decrease the term energies, respectively. Suprisingly, the term energies for configurations with f^6 and f^{13} occupation in Eu and Yb, respectively, are also reproduced reasonably well. However, empirical corrections had to be made in the corresponding AMOL calculations [29]. Probably this is due to the use of appropriate four-component numerical atomic orbitals in the present calculations.

The BDF results presented here even have a better accuracy than the large-scale scalar energy-consistent QR-PP [18] averaged coupled-pair functional calculations (ACPF) [54] with $(12s11p9d8f4g)/[9s8p6d5f4g]$ basis sets which were performed for comparison, e.g., their standard deviations from the spin-orbit averaged experimental data are 0.51 eV and 0.73 eV for Eu and Yb, respectively. The reliability of the relativistic density functional approach implemented in BDF has been demonstrated by the atomic calibration calculations. It is expected that results of the similar quality can be obtained for molecules provided that a comparable numerical accuracy is achieved.

3.2 Molecular calculations

To demonstrate the numerical stability of the present calculations with respect to the number of integration points, we performed three types of calculations on YbO(f^{14} $^1\Sigma^+$): the integration points (radial × angular) for Yb and O were chosen as (60 × 110, 40 × 110), (80 × 194, 60 × 110) and (100 × 194, 80 × 194), respectively. SCF calculations were performed at the LDASI level. Nonlocal corrections were then considered as perturbations. All spectroscopic constants were derived from a fourth-degree polynomial through five points of the potential curve with a spacing of 0.05 Å near the equilibrium distance. The obtained molecular total energies, dissociation energies, bond lengths and vibrational frequencies are given in Table 2. It can be seen

Table 2. Convergence of the total energies ΔE (au)[a], dissociation energies De (eV), bond lengths Re (Å) and vibrational frequencies ω_e (cm^{-1}) of YbO with respect to the number of integration points (radial × angular) of Yb and O: a = (60 × 110, 40 × 110); b = (80 × 194, 60 × 110); c = (100 × 194, 80 × 194); for other explanations, cf. Table 1

Method	Integration points	ΔE	De	Re	ω_e
		Nonrelativistic			
LDASI	a	0.00000	5.655	1.886	692
	b	−0.01669	5.647	1.890	672
	c	−0.01527	5.648	1.890	704
NLx	a	0.00000	4.417	1.943	632
	b	−0.01001	4.417	1.945	661
	c	−0.00858	4.414	1.943	630
NLc	a	0.00000	5.950	1.857	732
	b	−0.00984	5.939	1.855	727
	c	−0.00851	5.940	1.862	720
NLxc	a	0.00000	4.674	1.918	660
	b	−0.01669	4.670	1.923	645
	c	−0.01530	4.670	1.920	672
		Relativistic			
LDASI	a	0.00000	5.439	1.835	757
	b	−0.04745	5.433	1.839	750
	c	−0.05535	5.433	1.839	757
NLx	a	0.00000	4.349	1.888	686
	b	−0.04749	4.349	1.891	682
	c	−0.05539	4.349	1.890	685
NLc	a	0.00000	5.803	1.809	798
	b	−0.04746	5.795	1.812	790
	c	−0.05536	5.795	1.813	791
NLxc	a	0.00000	4.674	1.865	717
	b	−0.04750	4.671	1.868	710
	c	−0.05540	4.672	1.868	718

[a] The ΔE are relative to the corresponding energies of "a" at the internuclear distance of 1.90 Å

that although the total energies are only converged to 0.0015 au and 0.0079 au for nonrelativistic and relativistic calculations, respectively, the dissociation energies, which were obtained by the transition-state method [53], and the bond lengths are converged to 0.003 eV and 0.003 Å, respectively. The vibrational frequencies, which are more sensitive, have fluctuations of up to 30 cm^{-1}.

To achieve a sufficient numerical accuracy of results for all the molecules studied here, we used 100 × 194 and 80 × 194 for the lanthanide and chalcogen atoms, respectively. The calculated dissociation energies, bond lengths and vibrational frequencies for the molecular (ground) states of EuO($f^7\ {}^8\Sigma^-$), YbO($f^{14}\ {}^1\Sigma^+$), EuS($f^7\ {}^8\Sigma^-$) and YbS($f^{14}\ {}^1\Sigma^+$) are presented in Tables 3, 4, and 5, respectively. Experimental data [5–8] and other theoretical results, including QR-PP configuration interaction calculations [19–21] as well as the results derived from different versions of the Amsterdam density functional program package (i.e AMOL with relativistic first-order perturbation theory [28] and ADF with a self-consistent one-component relativistic treatment [56]), are also cited for comparison. Spin-orbit coupling and Stoll's SI corrections were accounted for in the AMOL [29] but not in the ADF [56] calculations. A comparison to the ADF results is still meaningful since the contributions of spin-orbit coupling to the dissociation energies of the molecular states studied here are not larger than 0.1 eV [57].

Table 3. Dissociation energies (in eV) for EuO($f^7\ {}^8\Sigma^-$), YbO ($f^{14}\ {}^1\Sigma^+$), EuS($f^7\ {}^8\Sigma^-$), and YbS($f^{14}\ {}^1\Sigma^+$). *BDF* present work; *AMOL* [29]; *ADF* [56]; *QR-PP* quasirelativistic pseudopotential [20, 21]; *Expt.* experimental values [5–8]; *LDA* local density approximation [40]; SI, self-interaction correction [41]; *NLx* nonlocal exchange correction [42]; *NLc* nonlocal correlation correction [43]; *NLxc* both nonlocal exchange and correlation corrections [41, 42]; *NR* nonrelativistic; *R* relativistic; *R-NR* relativistic corrections

Method		EuO			YbO			EuS			YbS		
		NR	R	R-NR	NR	R	R-NR	NR	R	R-NR	NR	R	R-NR
LDASI	AMOL	7.15	6.31	−0.84	5.89	5.04	–0.85						
LDASI	BDF	6.98	6.34	−0.64	5.65	5.43	−0.22	5.09	4.48	−0.61	4.30	3.75	−0.55
LDA	ADF	7.60	6.92	−0.68	6.15	5.85	−0.30	5.53	4.88	−0.65	4.73	4.20	−0.53
LDA	BDF	7.51	6.83	−0.68	6.12	5.76	−0.36	5.59	4.80	−0.79	4.67	3.94	−0.73
NLxSI	AMOL	6.07	5.19	−0.88	4.91	4.06	−0.85						
NLxSI	BDF	5.65	5.17	−0.48	4.42	4.35	−0.07	4.23	3.52	−0.71	3.39	2.81	−0.58
NLx	ADF	6.51	5.85	−0.66	4.84	4.83	−0.01	4.65	4.00	−0.65	3.92	3.26	−0.66
NLx	BDF	6.15	5.68	−0.47	4.86	4.65	−0.21	4.56	3.88	−0.67	3.67	3.02	−0.65
NLcSI	BDF	7.14	6.72	−0.42	5.94	5.80	−0.14	5.48	4.94	−0.54	4.64	4.21	−0.43
NLc	BDF	7.86	7.22	−0.64	6.43	6.12	−0.31	5.97	5.28	−0.69	5.01	4.35	−0.66
NLxcSI	BDF	5.94	5.55	−0.39	4.67	4.67	+0.00	4.58	3.99	−0.59	3.74	3.27	−0.47
NLxc	ADF	6.80	6.17	−0.63	5.13	5.16	+0.03	4.98	4.35	−0.63	4.15	3.63	−0.52
NLxc	BDF	6.46	6.04	−0.42	5.13	4.97	−0.16	4.90	4.32	−0.58	3.98	3.39	−0.59
QR-PP		4.68	3.92	−0.76		2.53[a]							
Expt.			4.96			4.33			3.71			2.73	

[a] The ground state of the *QR-PP* calculation is YbO ($f^{13}\sigma^1\ \ {}^3\Sigma^+(0^-)$) with 3.46 eV

Table 4. Bond lengths (in Å); for explanations see, Table 3

Method		EuO			YbO			EuS			YbS		
		NR	R	R-NR	NR	R	R-NR	NR	R	R-NR	NR	R	R-NR
LDASI	AMOL	1.87	1.84	−0.03	1.88	1.87	−0.01						
LDASI	BDF	1.88	1.85	−0.03	1.89	1.84	−0.05	2.41	2.38	−0.03	2.38	2.32	−0.06
LDA	ADF	1.85	1.84	−0.01	1.85	1.81	−0.04	2.37	2.35	−0.02	2.35	2.29	−0.06
LDA	BDF	1.86	1.85	−0.01	1.87	1.82	−0.05	2.39	2.37	−0.02	2.36	2.30	−0.06
NLxSI	AMOL	1.93	1.89	−0.04	1.94	1.93	−0.01						
NLxSI	BDF	1.94	1.90	−0.04	1.94	1.89	−0.05	2.47	2.44	−0.03	2.44	2.38	−0.06
NLx	ADF	1.90	1.89	−0.01	1.89	1.86	−0.03	2.41	2.41	−0.00	2.40	2.35	−0.05
NLx	BDF	1.92	1.90	−0.02	1.93	1.88	−0.05	2.44	2.43	−0.01	2.41	2.36	−0.05
LDASI	BDF	1.85	1.83	−0.02	1.86	1.81	−0.05	2.38	2.35	−0.03	2.35	2.29	−0.06
NLc	BDF	1.83	1.82	−0.01	1.84	1.79	−0.05	2.36	2.33	−0.03	2.33	2.27	−0.06
NLxcSI	BDF	1.91	1.88	−0.03	1.92	1.87	−0.05	2.44	2.42	−0.02	2.41	2.35	−0.06
NLxc	ADF	1.87	1.86	−0.01	1.87	1.84	−0.03	2.40	2.38	−0.02	2.35	2.32	−0.03
NLxc	BDF	1.89	1.87	−0.02	1.90	1.86	−0.04	2.42	2.40	−0.02	2.38	2.34	−0.04
QR-PP		1.91	1.92	+0.01	1.90	1.89[a]	−0.01						
Expt.			1.89			1.81			2.39[b]	(2.51)[b]		2.60[b]	

[a] The ground state of the *QR-PP* calculation is YbO ($f^{13}\sigma^1\ \ {}^3\Sigma^+(0^-)$) with 1.79 Å

[b] Empirically interpolated results. The values of 2.39 Å and 2.51 Å for EuS were derived from different interpolations [6]

Table 5. Vibrational frequencies (in cm^{-1}); for explanations, see Table 3

Method		EuO			YbO			EuS			YbS		
		NR	R	R-NR	NR	R	R-NR	NR	R	R-NR	NR	R	R-NR
LDASI	AMOL	710	726	+16	687	678	−9						
LDASI	BDF	705	742	+37	704	757	+53	385	388	+3	376	393	+17
LDA	BDF	724	750	+26	707	778	+69	398	398	+0	392	403	+11
NLxSI	AMOL	655	675	+20	623	615	−8						
NLxSI	BDF	647	685	+38	631	685	+54	358	360	+2	355	364	+9
NLx	BDF	674	691	+17	641	691	+50	373	368	−5	365	375	+10
NLcSI	BDF	741	770	+27	721	791	+70	401	407	+6	388	411	+23
NLc	BDF	749	783	+34	756	831	+75	413	418	+5	407	423	+16
NLxcSI	BDF	667	705	+38	672	718	+46	373	374	+1	365	379	+14
NLxc	BDF	695	714	+19	661	727	+66	386	383	−3	380	388	+8
QR-PP		702	702	+0		679[a]							
Expt.			672			699			400[b]				410[b]

[a] The ground state of the *QR-PP* calculation is YbO ($f^{13}\sigma^1\ {}^3\Sigma^+(0^-)$) with 884 cm^{-1}

[b] Empirically interpolated results

3.2.1 Dissociation energies. It can be seen from Table 3 that nonrelativistic LDA calculations overestimate the dissociation energies by about 2.0 eV for the molecules studied here. NLx corrections reduce the dissociation energies and thus the deviations are reduced to about 1.0 eV, whereas NLc corrections again increase the dissociation energies and therefore lead to larger discrepancies. Stoll's SI correction tends to reduce the dissociation energies by a few 0.1 eV. Relativistic corrections improve the dissociation energies drastically. However, the magnitudes of relativistic corrections are quite different at different levels of correlation treatment, reflecting the fact that relativistic effects and correlation effects are not additive for heavy element systems.

Although different basis sets were used, the present BDF results with and without SI corrections are in agreement with those of previous AMOL and ADF calculations, respectively. The NLx and SI corrected relativistic results are closest to the experimental values, the maximum absolute errors being less than 0.2 eV. The best level of theory applied here, i.e., BDF NLxcSI, gives dissociation energies in satisfactory agreement with the experimental values, i.e., EuO (calc. 5.55 eV, expt. 4.96 eV), YbO (calc. 4.67 eV, expt. 4.33 eV), EuS (calc. 3.99 eV, expt. 3.71 eV) and YbS (calc. 3.27 eV, expt. 2.73 eV).

3.2.2 Bond lengths. It is discernible from Table 4 that the BDF bond lengths are in good agreement with those of the previous AMOL and ADF studies. The well-known tendency of the LDA approach to underestimate bond lengths of metal-ligand bonds [31] is evident. NLx corrections tend to elongate the bonds, resulting in overestimations of bond lengths by several 0.01 Å, whereas NLc corrections shorten the bonds. SI corrections elongate the bonds by up to 0.02 Å. Relativistic effects are found to shorten the bonds only slightly. Thus, both NLx and NLc corrected relativistic results are usually in line with experimental data. The BDF NLxcSI results for EuO (1.88 Å) and YbO (1.87 Å) agree only for EuO with the experimental values (1.89 Å; 1.81 Å). It should be noted, however, that all calculations reported so far, i.e., BDF, AMOL, ADF and QR-PP, do not support the experimental bond length of 1.81 Å [8] for a $f^{14}\ {}^1\Sigma^+$ state of YbO. The bond length for EuS was estimated by empirical interpolation to be 2.39 Å and later corrected to be 2.51 Å [6]. The present calculations as well as the ADF results [56] are closer to 2.39 Å. In addition, the "experimental" value of 2.60 Å for YbS, derived in the same way as for EuS, also seems to be too long and should probably be revised. The value of 2.60 Å for YbS is also questionable because it is substantially larger than that of EuS, contradicting the usually observed lanthanoid contraction. The calculated bond lengths for YbO and YbS are slightly shorter than the corresponding values for EuO and EuS and are thus consistent with the expected lanthanoid contraction.

3.2.3 Vibrational frequencies. The BDF vibrational frequencies are in agreement with those from AMOL and ADF as well as QR-PP calculations as seen from Table 5. Nonlocal corrections influence the vibrational frequencies only modestly. Relativity also has no significant effects. Both NLx and NLc corrected relativistic results are in agreement with experimental data within an error bar of 30 cm^{-1}. At the NLxcSI level the BDF results for EuO (705 cm^{-1}) and YbO (718 cm^{-1}) are only slightly larger than the experimental values (672 cm^{-1}; 699 cm^{-1}). It is noteworthy, and at present unexplained, that although the BDF relativistic corrections found for EuO are similar to those from previous AMOL calculations, our values for YbO are substantially larger and of different sign.

3.2.4 Electronic structure and analysis of chemical bonding. In the following discussions, for the sake of simplicity, we will omit the difference in the terminology for nonrelativistic molecular orbitals (MOs) and relativistic molecular spinors (MSs). By comparing the energy levels and compositions of MOs for these molecules, the following features can be derived:

1. In the nonrelativistic approximation, the occupied MOs for EuO can be divided into three groups. The first group involves 10 orbitals which are located

within the range of -45 to -17 eV, and mainly consists of Eu 5*s*, 5*p* and O 2*s* orbitals. The second group involves six orbitals which are located within -5.5 to -4.5 eV. They are O 2*p* orbitals mixed to some extent with Eu 5*d* orbitals. The third group involves seven orbitals, namely Eu 4*f* orbitals. They are located within -4 to -3 eV. The LUMO mainly consists of the Eu 6*s* orbital.

Relativistic effects spread the energy ranges of the three groups of orbitals, but do not change the order of the MO energy levels. They lower the energy of the LUMO and thus result in a narrower HOMO-LUMO-energy gap, i.e., 0.43 eV, compared to the nonrelativistic value of 1.2 eV.

2. The feature of the nonrelativistic MOs for YbO is similar to that for EuO except that the group related to O 2*p* orbitals possesses higher energies than the Yb 4*f*-like group. However, spin-orbit interaction splits the Yb 4*f* group into three subgroups staggered with the O 2*p*-like group and shifts one subgroup ($4f_{7/2}$) to the frontier region; therefore the HOMO changes from O 2*p*-like to Yb 4*f*-like orbitals due to relativistic effects.
3. The MOs for EuS and YbS have similar features to YbO, that is, in the nonrelativistic approximation the MOs can be divided into three groups and the group related to the S 3*p* orbitals is located in the higher energy region, while relativistic effects split the Ln 4*f*-like MOs and shift a part of them to the frontier region.

The influence of relativistic effects on the electronic structure of lanthanide-containing compounds mainly exhibits itself in the MOs predominantly of Ln 4*f* character as summarized in Table 6. It can be seen that relativistic effects result in large spin-orbit splitting and promote the Ln 4*f*-like orbitals to the frontier region, which is in accordance with the fact that both Eu and Yb can readily form trivalent compounds , i.e., lose one *f* electron in addition to the two *s* electrons. The narrowing of the energy gaps between LUMOs and HOMOs must result in some changes in the molecular properties. Thus relativistic effects have to be taken into account for a correct description of the electronic structure and chemical bonding of lanthanide-containing molecules, especially when the ligands are also heavy elements.

Table 6. Relativistic effects on the lanthanide 4*f* orbitals. The nonrelativistic values are given in parentheses (in eV)[a]

Molecule	Center of MOs	Spin-orbit splitting	Primary HOMO	Components LUMO	Energy gap
EuO	-3.84	0.66	4*f*	6*s*	0.43
	(-4.00)		(4*f*)	(6*s*)	(1.19)
YbO	-4.58	1.36	4*f*	6*s*	0.43
	(-4.83)		(2*p*)	(6*s*)	(1.35)
EuS	-4.08	0.68	4*f*	6*s*	0.48
	(-5.43)		(3*p*)	(6*s*)	(0.70)
YbS	-5.11	1.41	4*f*	6*s*	0.47
	(-8.26)		(3*p*)	(6*s*)	(0.97)

[a] The center of gravity of the 4*f*-like MOs was calculated with the formulas: $E_{cent}(NR) = (E(4f_{\delta}) + E(4f_{\phi}))/2$, $E_{cent}(R) = (4E(4f_{5/2,5/2}) + 3E(4f_{7/2,5/2}))/7$. The spin-orbit splitting was calculated with the formula: $E_{so} = E(4f_{7/2,5/2}) - E(4f_{5/2,5/2})$. Here the notation of $4f_{j,m_j}$ was used

Atomic charges or valence states in molecules, as well as the participation of atomic valence orbitals in chemical bonding, are questions of interest to chemists. Mulliken population analysis [58] is probably the most widely used approach for a quantitative analysis. However, it suffers from a strong dependence on the basis sets. On the other hand, it becomes physically ambiguous to describe the contributions of "atomic orbitals" to chemical bonding with extended basis sets, because in that case a basis function does not correspond to an atomic orbital. These defects can be avoided by the introduction of AOIM, which are defined to be the eigenvectors of the system with the spherically averaged molecular potential field centered at the relevant atomic nucleus [32].

Table 7 presents the Mulliken population based on AOIM as well as the dipole moments and their derivatives. The atomic populations are very similar to those obtained by the AMOL [29]. Relativistic effects decrease the electronic population on Ln 5*d* and 4*f* orbitals, whereas they increase the population on Ln 6*s* and 6*p* orbitals, in accordance with the fact that relativity stabilizes the Ln 6*s* and 6*p* orbitals while it destabilizes the Ln 5*d* and 4*f* orbitals. The population on the Ln 6*s* orbital is less than one and that on the 5*d* orbitals is

Table 7. Mulliken population analysis, covalency and dipole moments at the relativistic LDA level. The nonrelativistic values are given in parentheses. X_α, SCF, CI results are cited from Table IX of Ref. [29]

		EuO	YbO	EuS	YbS
Ln	4*f*	6.83	13.71	6.93	13.92
		(7.05)	(13.95)	(7.03)	(13.99)
	5*d*	1.03	0.90	0.97	0.62
		(1.08)	(1.04)	(1.05)	(0.87)
	6*s*	0.28	0.44	0.36	0.76
		(0.01)	(0.04)	(0.15)	(0.45)
	6*p*	0.17	0.20	0.17	0.20
		(0.10)	(0.17)	(0.14)	(0.17)
L	*ns*	1.90	1.90	1.91	1.92
		(1.93)	(1.93)	(1.90)	(1.91)
	np	4.73	4.79	4.61	4.57
		(4.79)	(4.83)	(4.70)	(4.60)
Charges	LDA	±0.68	±0.74	±0.58	±0.51
		(±0.75)	(±0.78)	(±0.66)	(±0.53)
	X_α	±0.66	±0.62		
		(±0.72)	(±0.79)		
	SCF	(±1.04)	(±1.13)		
Covalency(%)[a]		66.0	63.0	71.0	74.5
		(62.5)	(61.0)	(67.0)	(73.5)
Dipole μ[D]	LDA	5.23	5.59	7.77	7.17
		(6.77)	(7.38)	(8.96)	(8.99)
	X_α	(6.57)	(7.23)		
	CI	(9.18)	(10.93)		
$d\mu/dR$ [D/Å]	LDA	9.74	7.18	6.16	4.92
		(9.33)	(10.15)	(6.04)	(4.95)
	X_α	(11.8)	(6.5)		
	CI	(10.9)	(8.6)		

[a] The covalency is defined as (1-net charge/2)

about one, indicating that about one electron is promoted from the Ln 6*s* to the 5*d* orbitals in the molecular formation process. It is interesting to note that the relativistic decrement of the dissociation energy (see Table 3) might be ascribed to such an electronic promotion. From the calculations on the europium atom it is found that the energy difference between the two configurations $4f^7 5d^1 6s^1$ and $4f^7 6s^2$ is nonrelativistically 0.84 eV and relativistically 1.37 eV (see Table 1), i.e., relativity increases the promotion energy for transferring one electron from Eu 6*s* to 5*d* by about 0.5 eV. For ytterbium the corresponding relativistic increment for the electron promotion, i.e., the energy difference between Yb $4f^{14} 5d^1 6s^1$ and $4f^{14} 6s^2$ is as large as 0.8 eV (see Table 1). Therefore, relativity may be one of the reasons causing heavier lanthanide atoms to possess weaker bonding potentials than the lighter ones.

The net charges on the metals are less than one, indicating a strong covalency in these molecules. From oxygen to sulfur the net charges on metals are reduced by $0.1 \sim 0.2$e. The covalency given in Table 7, which was calculated according to Pauling's definition of bond ionicity, namely, covalency $= (1-$ net charges/2), shows that polarized covalent bonds exist and relativity increases the bond covalency slightly.

The dipole moments are reduced by relativity due to the relativistic shortening of the bond lengths and the slight reduction of the net charges on metals. The moment derivatives of roughly 10 $D/\mathrm{\AA}$ for EuO and YbO might indicate dynamical charges of 2e on EuO and YbO as already mentioned by Wang et al. [29], whereas the moment derivatives for EuS and YbS are much smaller. The gross Mulliken and Mayer bond orders [59] based on AOIM are given in Table 8. The Mayer bond orders are close to the conventional values of bond multiplicity and are numerically more stable than the Mulliken bond orders [32]. So the partial contributions of atomic orbitals to the gross Mayer bond orders are preferred to be a criterion to judge the bonding potential of related atomic orbitals. The following orders can be derived from Table 8: $5d > 6p > 4f > 6s$ for EuO, $5d > 6p > 6s > 4f$ for YbO, $5d > 6s > 6p > 4f$ for EuS and $5d > 6s > 6p > 4f$ for YbS. Relativity decreases the contributions of the Ln 5*d* orbitals while it increases those of the 6*s*, 6*p* and 4*f* orbitals to a different extent. For YbS the relativistic increment of the 6*s* orbital contribution is significant.

Table 8. Partial contributions of lanthanide atomic orbitals to Mulliken and Mayer bond orders based on AOIM [32]. The nonrelativistic values are given in parentheses

		EuO	YbO	EuS	YbS
Mulliken bond orders		1.17	1.27	1.42	1.19
		(1.03)	(1.14)	(1.32)	(1.14)
Partial contributions(%)	4*f*	5.0	0.9	1.7	0.8
		(4.1)	(0.3)	(1.8)	(0.0)
	5*d*	74.7	68.1	62.9	51.6
		(83.5)	(75.9)	(81.8)	(61.8)
	6*s*	5.3	11.1	18.8	27.3
		(0.6)	(3.4)	(16.1)	(19.6)
	6*p*	12.8	19.9	16.6	20.2
		(11.8)	(21.0)	(17.3)	(18.6)
Mayer bond orders		2.06	2.04	2.19	2.26
		(1.95)	(1.96)	(2.16)	(2.20)
Partial contributions(%)	4*f*	9.0	3.6	3.6	2.2
		(7.5)	(1.4)	(3.6)	(0.2)
	5*d*	73.7	68.5	66.3	45.6
		(80.5)	(80.8)	(73.8)	(59.8)
	6*s*	4.2	12.2	16.5	37.0
		(1.0)	(1.5)	(8.8)	(27.5)
	6*p*	11.7	15.0	12.2	15.0
		(7.7)	(14.6)	(11.2)	(12.5)

4 Conclusions

A new relativistic four-component density functional program package, BDF, that can deal with total-energy-related chemical properties of systems containing heavy elements has been developed and was shown to give reliable results for lanthanide atoms and diatomic molecules. The present work shows that modern (nonrelativistic) density functionals also perform reasonably well for inner 4*f* shells of lanthanide systems within the fully relativistic framework. Of course, further applications to other (lanthanide) elements and their compounds have to be made to make a final judgement.

Relativistic effects influence the bond lengths and vibrational frequencies of the molecules studied here only modestly, whereas they improve the dissociation energies drastically. The relativistic decrement of dissociation energies can be correlated to the electron promotion from the Ln 6*s* to the 5*d* orbitals in the molecular formation processes.

The calculated spectroscopic constants for YbO (f^{14} $^1\Sigma^+$) coincide with the latest experimental data for the ground state of YbO only in the case of dissociation energy and vibrational frequency, whereas a longer bond length is obtained in agreement with other theoretical investigations. According to the present calculations, the "experimental" bond lengths for EuS and YbS, which were derived from empirical interpolations, seem to be too long and need to be revised.

The Ln 4*f* orbitals are essentially localized. The bond orders are mainly contributed by the interaction between the Ln 5*d* and ligand *np* orbitals. The contribution to bond orders by the lanthanide atomic orbitals is in the order of $5d > 6s \sim 6p > 4f$. Relativistic effects decrease the bonding potential of 5*d* orbitals while they increase that of 6*s*, 6*p* and, to a lesser extent, 4*f* orbitals. However, the order of bonding potential remains unchanged. Relativistic effects increase the covalency of the molecules studied here, which is parallel with the relativistic population increase on the Ln 6*s* and 6*p* orbitals.

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