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The performance of density functional theory for LnF (Ln = Nd, Eu, Gd, Yb) and YbH

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Abstract. Different density functional theory (DFT) functionals have been evaluated by studying geometries and bond strengths of YbH, YbF, EuF, GdF, and NdF and compared with accurate CCSD(T) results and, when available, experiment. The agreement between the CCSD(T) results and experiment, when available, is good. The agreement is also good between bond strengths calculated at the DFT level using relativistic effective core potentials and the CCSD(T) results. However, the all-electron ADF calculations systematically overestimate binding energies. The geometries obtained by both the all-electron and the effective-core-potential-based DFT calculations are generally in good agreement with the CCSD(T) results.

Keywords: Density functional theory – Coupled-cluster theory – Lanthanides – Lanthanide diatomics – Relativistic effects

Introduction

Two decades ago there was a general belief that lanthanides did not form stable organometallic compounds [1]. However, since then considerable new knowledge has been gained about the peculiar properties and rules of this type of chemistry [1, 2, 3], and lanthanide chemistry has become a rapidly developing field. It turns out that the organometallic chemistry of the lanthanides is quite different from that of, for example, the *d*-block transition metals. Owing to the possible use as one-component catalysts for olefin polymerization [4] and corresponding industrial importance, there has, in particular, been much focus on lanthanide metallocenes [2, 3].

Quantum chemical modeling has become a frequently used tool in studies of the organometallic chemistry of main-group and transition-metal elements [5, 6, 7, 8, 9]; however, for heavy elements such as the lanthanides, the methodology is less firmly established. Method evaluation is more difficult than for the lighter elements owing to the scarcity of experimental thermochemical data. Furthermore, theoretical studies are complicated owing to the presence of partially filled *f* shells which in many cases give rise to a large number of low-lying states and important spin–orbit (SO) coupling effects.

In general, organometallic complexes have large and bulky ligands which prohibit the use of established accurate ab initio methods. This problem may be circumvented by modeling the complexes by simpler idealized model systems which still carry the important features of the original complex; however, even these simplified models are usually quite large and it is important to determine the accuracy of more approximate methods.

Density functional theory (DFT) has been proven to give good accuracy at low cost for molecules of many elements. A number of different functionals have been suggested [9, 10, 11, 12, 13, 14, 15, 16], most of which perform quite well for many molecular properties. The hybrid B3LYP [15] functional is significantly more reliable than BLYP [10, 11] for atomization energies of the lighter elements. The BLYP functional has in turn been found to be superior to the BP86 [11, 13, 14] and BP [11, 12, 13] functionals. Average deviations from experiment of 2, 5, 10, and 12 kcal/mol, respectively, were found by Bauschlicher [17] for 55 first-row and second-row compounds [18]. In the same study all the functionals gave reasonable geometries. Kock and Holthausen [9] reviewed the performance of many functionals and their work is recommended as a comprehensive overview of DFT and its applications. Note that calculation of the

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atomization energy represents a worst-case situation with respect to accuracy for bond energies. Reaction energies may be expected to show significantly better accuracy owing to cancellation of errors. The accuracy of the various functionals is less obvious for transition metals, partly because there are not so many binding energies of transition-metals systems that are accurately known compared to the first-row and second-row elements. However, several studies [9, 19] indicate that B3LYP is a reliable functional for both geometries and energies. The BLYP functional appears to be equal to or better than the BP86 functional for energies, and these features agree with the trend observed for the first-row and second-row molecules. B3LYP and BP86 seem to give geometries of similar quality, while BLYP sometimes gives poorer results.

For elements as heavy as the lanthanides and actinides, it is necessary to include a proper treatment of relativistic effects. Currently the highest level of relativistic treatment in quantum chemistry is the four-component methods based on the Dirac equation [20, 21, 22, 23], but reasonable accuracy may also be obtained by a number of more approximate methods [24, 25, 26]. First-order perturbation theory has been shown to be quite accurate for elements as heavy as the second-row transition elements, but the operators are not variationally stable. This approach is thus not reliable for systems containing heavy elements. Several variationally stable methods have been proposed: The Douglas–Kroll (DK) method [27, 28, 29], which has been used successfully in ab initio calculations since the early 1990s [30], and the zero-order regular approximation (ZORA) developed by van Lenthe and coworkers [31, 32, 33], which have been used mainly in DFT studies. The quasi-relativistic approximation has been used for lanthanide compounds by Wang and coworkers [34, 35] and Willson and Andrews [36]. Lately the DK method has also been employed in DFT studies [37, 38]. Hong et al. [38] compared the ZORA and the DK approaches at the scalar-relativistic DFT level (for diatomics with La, Lu, Ac, and Lr), and they found very consistent bond lengths and binding energies.

Theoretical calculations on heavy elements usually include some kind of core approximation, either (in DFT calculations) by freezing the core orbitals in their atomic shape [34], or by replacing the core with a (relativistic) effective core potential [(R)ECP] which mimics the potential of the electron core (and include relativistic effects). The RECPs for the lanthanides have been developed and thoroughly tested by Dolg and coworkers [26, 39, 40, 41, 42].

Hay and Martin [43] have presented a systematic study of geometries and vibrational frequencies of the actinide complexes UF_6, NpF_6, and PuF_6 using RECPs and DFT. They reported that the B3LYP functional gives better results than BLYP both for geometries and vibrational frequencies, while bond dissociation energies were not studied.

The present study is an attempt to evaluate the performance of different DFT approaches [9] in quantum chemical studies of lanthanide compounds, comparing with experimental results as well as all-electron coupled-cluster ab initio calculations [with single, double, and noniterative triple corrections, CCSD(T)]. We chose to investigate the inorganic diatomics LnF (Ln = Nd, Eu, Gd, Yb) and YbH for which many relevant experimental data are available. We focus on the performance of the BP86, BP, BLYP, and B3LYP functionals (see Table 1 for definitions). We are not aware of any previous systematic study that compares these functionals for the lanthanides.

Computational details

For the ab initio calculations we used the highly accurate CCSD(T) method, employing the MOLCAS 5.0 [44] program package. Scalar-relativistic effects were described at the one-electron level by means of the DK transformation [27]. The triples corrections for CCSD(T) were calculated noniteratively according to Watts et al. [45] for open-shell systems, and according to Raghavachari et al. [46] for closed-shell systems. The electrons in the orbitals 4*f*, 5*p*, 5–6*s* for Ln, the 2*s* and 2*p* for F, and the 1*s* of H were kept active, unless otherwise stated.

The all-electron lanthanide basis sets were obtained as follows. Faegri's [47] relativistic (23s, 19p, 14d, 9f) dual family basis sets were modified by replacing the four (two) low exponent s (p) functions with five (four) functions in an even-tempered series (ratio 2.5). An extra low-exponent d- and f-type function was also added giving (24s, 21p, 15d, 10f) basis sets that subsequently were contracted by optimization at the Hartree–Fock (HF) level to give [9s, 8p, 6d, 4f]. These basis sets are close to basis-set-limit quality in the s, p, d, and f space and without gaps in the exponent range in the valence region. They may be obtained from the authors upon request. A set of three even-tempered g functions (ratio of $\sqrt{5}$) was added and optimized at the CCSD(T) level, giving final basis sets of size (24s, 21p, 15d, 10f, 3g) → [9s, 8p, 6d, 4f, 3g]. The optimal degree of contraction was thoroughly tested for Yb in YbH and YbF at the CCSD(T) level. The g functions proved to have only a marginal effect on the bond strength of YbH (0.8 kJ) but were important for YbF (around 17 kJ). For the sake of consistency, we chose to use the same basis set for both systems including the g functions. Fluorine and hydrogen were described by the Dunning correlation-consistent polarized valence triple zeta (cc-pVTZ) [48] basis sets (basis set cc-pVTZ for F and H). The geometries were optimized by stepping the bond distances and bracketing the minima within 0.005 Å.

Table 1. Definitions of the functionals employed

Functional	Software	Local		Gradient	
		Exchange	Correlation	Exchange	Correlation
BLYP	ADF, Gaussian98	Slater	LYP [10]	Becke [11]	LYP [10]
BP	ADF	Slater	VWN [12]	Becke	Perdew86 [13]
BP86	Gaussian98	Slater	Perdew81 [14]	Becke	Perdew86
B3LYP [15]	Gaussian98	Slater + HF	LYP–VWN	Becke3	LYP

Table 2. Terms and constants for atoms and molecules. Atomic configurations and symmetries are taken from Ref. [60]. Molecular symmetries and configurations are based on the work of Gotkis [55]

Atom	Configurations	Symmetry	Molecule	Configurations	Symmetry
Nd	$4f^4 6s^2$	^{5}I, see text	NdF	$\mathrm{Nd}^+[4f^4(\sigma_{6s,6p})]\mathrm{F}^-$	$^6A_2$, see text
Eu	$4f^7 6s^2$	^{8}S	EuF	$\mathrm{Eu}^+[4f^7(\sigma_{6s,6p})]\mathrm{F}^-$	$^9\Sigma^-$
Gd	$4f^7 5d^1 6s^2$	^{9}D, see text	GdF	$\mathrm{Gd}^+[4f^7(\sigma_{6s,6p})^2]\mathrm{F}^-$	$^8\Sigma^-$
Yb	$4f^{14} 6s^2$	^{1}S	YbF	$\mathrm{Yb}^+[4f^{14}(\sigma_{6s,6p})]\mathrm{F}^-$	$^2\Sigma^+$
			YbH	$\mathrm{Yb}[4f^{14}](\sigma_{\mathrm{H}1s}{}^2\sigma_{6s,6p})]$	$^2\Sigma^+$

The DFT methods applied represent different relativistic DFT approaches and were calculated either with the ADF [49] or the Gaussian98 program [50]. In the Gaussian98 calculations the scalar-relativistic effects were taken care of by RECPs of the Stuttgart–Dresden–Bonn variety. Two types of RECPs with either a small [40, 51] or a large core [41, 42] were employed. The basis sets for the large-core RECPs were extended with functions from the optimized all-electron basis set, adding the three most diffuse f functions and the second most diffuse g function. The cc-pVTZ [48] basis set was used for F. In the large-core calculations the hydrogen basis set was taken from van Duijneveldt's [52] 5s basis contracted to 3s at the HF level and augmented with a p function with exponent 0.8. In the small-core calculations the cc-pVTZ [48] was used for H. The functionals employed are described in Table 1.

In the ADF calculations two different relativistic approaches were applied, the quasi-relativistic (first-order Pauli Hamiltonian) [31, 53], and the ZORA [32, 33] approach. The latter approach includes corrections in order to fulfill gauge invariance [33]. A frozen-core approximation including the 4*s*, 4*p*, and 4*d* orbitals was used for the lanthanide atoms with basis sets of TZV quality.[1] F and H were represented with all-electron basis sets of TZV quality and one polarization function. Definitions of the functionals are given in Table 1. The BP functional was used because the BP86 functional is not implemented in ADF; however, they yield similar results [17] and BP differs from BP86 only in the local part of the functional where the parameterization of Vosko, Wilk, and Nusair (VWN) is employed instead of Perdew81.

The computational approach in ADF differs in several ways from that in Gaussian98: in ADF we use frozen-core orbitals in all-electron calculations, while RECPs are employed in Gaussian98. The RECPs include the scalar-relativistic effects and no further relativistic treatment is performed. In ADF the scalar-relativistic effects are explicitly taken into account in the Hamiltonian by either the quasi-relativistic (using the mass-velocity and Darwin operators iteratively with suitable boundary conditions) or the ZORA approach. The use of frozen core versus RECPs obviously also leads to use of different basis sets, and while g functions were included for angular polarization in the Gaussian98 calculations, these functions are unavailable in ADF. ADF applies Slater functions, while Gaussian functions are used in Gaussian98 as in most other quantum chemical codes. Unrestricted and restricted DFT spin calculations were performed for open-shell and closed-shell systems, respectively.

Results and discussion

The experimental ground states, both for the diatomic molecules and for the isolated atoms, are given in Table 2. Technically, the Molcas calculations on the diatomic molecules and atoms were done in C_{2v} symmetry, with the exception of Eu and Yb, for which we used the D_{2h} symmetry (since Eu has a half-filled *f* shell and Yb has a full *f* shell this does not influence the results).

The Gaussian98 calculations were done in D_{2h} symmetry for the atoms and in C_{2v} symmetry for the diatomics. The full K_h and $C_{\infty v}$ symmetries were used in the ADF calculations.

Bond lengths

Our calculated CCSD(T) bond lengths, given in Table 3, are in excellent agreement with the experimental results as well as the counterpoise-corrected CCSD(T) and single reference configuration interaction including single and double excitations and Davidson's correction (CISD + Q) results of Cao et al. [54]. Typical deviations are 0.01 Å. The experimental bond length of NdF is unavailable, but our CCSD(T) result of 2.09 Å may indicate that the value of 2.12 Å estimated by Gotkis [55] is somewhat too high.

The DFT bond length calculations performed with small-core ECPs in Gaussian98 agree very well with the CCSD(T) results and experimental values. Corresponding calculations with large-core ECPs give in all cases bond lengths that are too long (0.01–0.07 Å) relative to experimental values. The B3LYP and BP86 functionals give very similar results. The BLYP functional overestimates the bond lengths slightly more than B3LYP and BP86 in all cases. This agrees well with the results for actinide complexes presented by Hay and Martin [43].

We find the same tendency for the ADF results where the BLYP functional gives (typically 0.02 Å) longer bond lengths than the BP functional in all cases; however, the deviations from experiments are very similar for the two functionals. Employing the quasi-relativistic approach rather than ZORA (with the BLYP functional) gave bond lengths 0.01–0.02 Å shorter.

The lack of g functions in ADF has probably only marginal effects, since employing the small-core basis set without g functions in Gaussian98 calculations reduced the bond lengths by only 0.01 Å or less.

Wang and Schwarz [34] reported bond lengths for YbH, YbF, and GdF from quasi-relativistic DFT calculations. Their GdF result agrees excellently with the experimental value, while the other two bonds are somewhat (0.03–0.08 Å) too long. The local density approximation (LDA) was applied in these calculations with correlation corrections of Vosko et al. [12] and Stoll et al. [56] and exchange correction of Becke [11]. The calculations were performed with the AMOL program. Four-component DFT results for YbH, YbF [57], and

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[1] Basis sets from the library of ADF2000.02. Quasi-relativistic approach: IV/Ln.4d, Ln = Nd, Eu, Gd, Yb, IV/F and IV/H. Zora approach: ZORA/V/Ln.4d, Ln = Nd, Eu, Gd, Yb

Table 3. Calculated and experimental ground-state bond lengths, r_e, given in angstroms. The density functional theory (*DFT*) and ab initio results were generated as indicated in Sect. 2, employing the Gaussian98 program (*G98*) with small-core (*sc*) and large-core (*lc*) effective core potentials (*ECPs*), and the ADF code with the Pauli approximation and the zero-order regular approximation (*ZORA*) for treating relativistic effects. Earlier theoretical results are also given

	YbH	YbF	GdF	EuF	NdF
Experimental	2.0526 [64]	2.0165 [78]	1.959 [79][a]	2.083 [80, 81][b]	2.12 [55][c]
CCSD(T)	2.06	2.03	1.97	2.08	2.09
B3LYP G98 scECP	2.07	2.02	1.99	2.07	2.08
BLYP G98 scECP	2.06	2.01	2.00	2.08	2.09
B3LYP G98 lcECP	2.11	2.05	1.97	2.10	2.13
BLYP G98 lcECP	2.12	2.06	1.99	2.11	2.14
BP86 G98 lcECP	2.11	2.04	1.98	2.09	2.12
BLYP ADF Pauli	2.02	2.00	2.00	2.09	–
BLYP ADF ZORA	2.04	2.02	2.01	2.10	2.10
BP ADF ZORA	2.03	2.00	1.99	2.07	2.08
DFT, Wang and Schwarz[d]	2.08	2.07	1.96	–	–
Ab initio, Cao et al. [54][e]	2.072	2.034	1.963	2.088	–
Four-component DFT[f]	2.033 [57]	1.987 [57]	1.996 [21]		

[a] Calculated from rotational constants of ^{156}GdF from Ref. [79]

[b] r_0 value from Ref. [80]. See also Ref. [81]

[c] Estimated/interpolated value from Ref. [55]

[d] DFT results [34] including correlation correction of Vosko et al. [12] and Stoll et al. [56] and exchange correction of Becke [11]

[e] Basis set superposition error corrected CCSD(T) (YbH) and CISD + Q (YbF,GdF, and EuF) results employing sc ECPs [54]

[f] Fully relativistic four-component DFT calculation by Dolg and coworkers [21, 57], with the local density approximation, self-interaction of Stoll and coworkers [56, 58], exchange correction of Becke [11], and correlation correction of Perdew [13] (GdF) or the same corrections except the Perdew–Wang formula [59] was employed within the local density approximation (YbH and YbF)

GdF [21] by Dolg and coworkers are also shown in Table 3, and they agree very well with experimental results. These four-component DFT results were calculated with the LDA, correlation corrections of Stoll and coworkers [56, 58] and Perdew [13], and exchange correction of Becke [11] for GdF. The same corrections were used for YbH and YbF except the Perdew–Wang formula [59] was employed within the LDA. (The profusion of subtly different functionals mentioned in this article may serve as an illustration of the fundamental conceptual difference between DFT and ab initio methods.)

Dissociation energies

In the present evaluation of different functionals and DFT approaches we have not included a proper treatment of SO effects in the computational methods. This will not affect the comparison between DFT and CCSD(T) results, but may be important for comparison with experimental results. SO effects will only have a significant influence on the energies of Gd, Nd, and NdF. The SO energy correction for Gd, obtained from the energy difference between the ground state $^9D_2$ and the Landé averaged energy of the “associated” *j* levels, is 10.5 kJ. Taking the weighted average of the Landé levels should in this case provide a good estimate of the spin-free energies, since the interaction with other states is weak (the sums of the weights of the relevant *j* levels were found to be 92% or greater [60]). In the case of NdF, the SO coupling is active both in the molecule and in the Nd atom. The experimental spectrum of NdF is, as far as we know, unavailable.

We calculated the SO effect in Nd and NdF using the eight lowest configurations per symmetry obtained by distributing four electrons in seven atomic *f* orbitals for Nd and five electrons in the seven *f* orbitals and the open σ orbital in NdF (Table 2). The energy difference between the spin-free state and the lowest root in the SO calculation was 23 kJ/mol for Nd and 35 kJ/mol for NdF. The difference between the $^5I_4$ term in the experimental spectrum of Nd and the Landé-averaged energy is 34 kJ/mol, in fair agreement with our self-consistent-field result. The larger SO effect obtained by us for the diatomic molecule may be due to the additional open shell compared to the atom or it may be due simply to the low accuracy. In any case, these results permit us to conclude that the SO effect on the dissociation energy of NdF is minor.

The CCSD(T) method is a single-reference method and may be inefficient for systems with large nondynamical correlation effects. Lee and Taylor [61] have formulated a diagnostic approach for simple identification of potential difficulties with nondynamical correlation in CCSD(T) for closed-shell systems, by taking the norm of the single-excitation cluster amplitudes ($||t_1||$) in the CCSD wave function, scaled to be independent of the number of correlated electrons (N): $T_1 = ||t_1||/\sqrt{N}$. It has been suggested [62] that $T_1 > 0.08$ indicates that the CCSD(T) results should be regarded with caution. Examination of the individual amplitudes should also be included in the evaluation of the quality. Even though this is formulated for closed-shell systems, we assume this also has at least a qualitative relevance for open-shell systems. Our T_1 diagnostic for the open-shell systems is based on the $\underline{t}_{1,\alpha}$ value (greater than $t_{1\beta}$). All the atoms and molecules, except Nd and NdF, have a

Table 4. Calculated and experimental ground-state bond dissociation energies, D_e(kJ/mol). The DFT and ab initio results were generated as indicated in Sect. 2, employing the G98 program with sc and lc ECPs, and the ADF code with the Pauli approximation and the ZORA for treating relativistic effects. Earlier theoretical results are also given. Experimental D_e values were generated from the experimental D_0 values corrected with zero-point energies (*ZPEs*). The ZPEs were estimated from experimental vibrational frequencies. Basis set superposition error in the CCSD(T) results was estimated to be 3 kJ or less for YbH and approximately 10 kJ for LnF (corrections not included)

	YbH	YbF	GdF	EuF	NdF
Experimental	≤ 157 or ≤ 194 [64]	≈470 [69] or ≥520 ± 10 [64, 68]	590 ± 17 or 674 ± 17 [64, 65][a]	542 ± 8 [63][b]	569 ± 13 [64, 67]
Experimental ω_e	1250 [64]	502 [64]	607 [79]	493 [80, 81]	483[c]
CCSD(T)	133	465	614[d]	525	545
B3LYP G98 scECP	150	492	637[d]	532	557
BLYP G98 scECP	151	516	665[d]	549	579
B3LYP G98 lcECP	144	485	660	530	550
BLYP G98 lcECP	143	501	680	547	567
BP86 G98 lcECP	154	512	681	558	578
BLYP ADF Pauli	172	568	714[d]	586	–
BLYP ADF ZORA	151	538	730[d]	590	628
BP ADF ZORA	165	553	737[d]	612	650
DFT, Wang and Schwarz[e]	152	500	565	–	–
Ab initio, Cao et al.[f]	144	504	602	541	–
Four-component DFT[g]	144	539	705		

[a] Results of Ref. [65] (590 ± 17 kJ7 mol) have been reevaluated by Huber and Herzberg [64] (674 ± 17 kJ/mol)

[b] See also Refs. [64, 65, 66]

[c] Estimated/interpolated value from Ref. [55]

[d] Spin–orbit energy correction included

[e] DFT results [34] including correlation correction of Vosko et al. [12] and Stoll et al. [56] and exchange correction of Becke [11]

[f] Basis set superposition error corrected CCSD(T) (YbH) and CISD + Q (YbF,GdF, and EuF) results employing sc ECPs [54]

[g] Fully relativistic four-component DFT calculation by Dolg and coworkers [21, 57], with the local density approximation, self-interaction of Stoll and coworkers [56, 58], exchange correction of Becke [11], and correlation correction of Perdew [13] (GdF) or the same corrections except the Perdew–Wang formula [59] was employed within the local density approximation (YbH and YbF)

$T_1 \leq 0.03$ and reasonably low single- and double-excitation amplitudes (0.09 or less). For NdF the $T_1 = 0.06$ and the maximum single-excitation amplitude is 0.11. For Nd $T_1 = 0.03$ and is fine, but a double-excitation amplitude of 0.13 may indicate that the calculated bond strength of NdF should be regarded with some caution. For the other bond strengths we conclude that CCSD(T) performs appropriately for our purpose.

In the cases where experimental error limits for dissociation energies have been indicated in the original articles, these limits have been included in Table 4. However, experimental studies on these compounds are quite complicated, and the parameters derived (such as D_e) are in some cases necessarily based on specific interpretations and assumptions about the experimental results. For EuF, the most recent experimental value of $D_e = 542 \pm 8$ kJ/mol [63] finds support in several earlier studies [64, 65, 66], while for NdF only a single, more than 30-year-old, study reports $D_e = 569 \pm 13$ kJ/mol [64, 67]. For YbH only upper limits for D_e are available [64]. A lower limit $D_e \geq 520 \pm 10$ kJ/mol [68] does not agree well with a rather approximate value of $D_e \approx 470$ kJ/mol [69] for YbF [64]. Finally, for GdF, the experimental result $D_e = 590 \pm 17$ kJ/mol of Zmbov and Margrave [65] has been questioned by Huber and Herzberg [64], since a reevaluation of D_e on the basis of the data of the original publication [65] gives $D_e = 674 \pm 17$ kJ/mol [64].

The evaluation of the computational approaches with respect to dissociation energies is more difficult than for bond lengths owing to less accurate and in some cases possibly misinterpreted or poorly understood experimental data as discussed earlier. However, the agreement between our CCSD(T) and the experimental results is encouraging. For YbF, EuF, and NdF our CCSD(T) results are slightly smaller, but within 95% of experiment. The experimental lower limit $D_e \geq 520 \pm 10$ kJ/mol for YbF [68] appears to be too high. Also the CCSD(T) value for GdF agrees within error bars with the original experimental $D_e = 590 \pm 17$ kJ/mol of Zmbov and Margrave [65]. The quality of the scalar-relativistic DK operators was tested by comparing HF calculations with relativistic four-component Dirac–HF calculations. The agreement was excellent, and on the basis of this result the relativistic DK approach was ruled out as a possible source of significant errors.

The basis set superposition error (BSSE) was checked for YbF at the CCSD(T) level, by calculating the energy for the separate atoms with the basis set of the other atom localized as in the optimized YbF geometry. We found that the total BSSE of 10 kJ is dominated (70%) by the effect on the F energy. Since the contribution from Yb is rather small in comparison, it is likely that the total BSSE will be similar for the other computed fluorides and possibly even smaller owing to fewer *f* electrons. The BSSE for YbH was estimated to be 3 kJ or less.

Cao et al. [54] reported (counterpoise-corrected) CISD + Q results for YbF, GdF, and EuF, and CCSD(T) results for YbH, which agree very well with experimental results considering the error margins. Taking our estimated BSSE correction of 10 kJ into account, we get 130, 455, 604, and 515 kJ/mol for YbH, YbF, GdF, and EuF, respectively, while Cao et al. reported 144, 504, 602, and 541. A large number of electrons, (Ln 20 + 4*f* electrons, F seven electrons), are correlated in the CISD + Q calculations, a computational method which is known to lack size-extensivity in contrast to CCSD(T). In our opinion the CCSD(T) results should be somewhat more accurate than the CISD + Q results, but it is, however, difficult to gauge the relative accuracy of these approaches.

DFT results obtained with the Gaussian98 program agree very well with our CCSD(T) and with experimental results, particularly when the B3LYP functional is used, which gives typical deviations from CCSD(T) of 5–20 kJ. The largest discrepancy, relative to CCSD(T), 67 kJ/mol, is found for the bond strength of GdF calculated with the BP86 functional and large-core ECPs.

We have seen that small-core ECPs generally give bond lengths a few picometers shorter than large-core ECPs. In these cases, the small-core ECPs usually also give somewhat larger dissociation energies. However, our calculated energies are surprisingly independent of core size compared to the difference in calculated bond lengths, considering that less rigorous models are usually needed to reproduce geometries as compared to energies. Wang and Dolg [70] have reported that the performance of large-core ECPs is improved when core-polarization potentials are included.

Our results show a systematic trend for the three functionals that were applied in the DFT calculations. BP86 gives stronger bonds than BLYP, while B3LYP gives the weakest bonds. The latter deviates least from the CCSD(T) results and generally yields the best agreement with experimental values. The same trends in performance (with respect to deviations) for these functionals have also been reported for first-row and second row systems as well as for transition elements [9, 17] (see Introduction). The BP86 functional overbinds considerably and deviates the most from experimental and CCSD(T) values. It is worth mentioning that another hybrid functional, B3PW91, has recently shown very promising and competitive results compared to B3LYP, and may be recommended for lanthanides [71].

The ADF results using either the quasi-relativistic or the ZORA approach largely overbind the fluorides (by 60–120 kJ) relative to our CCSD(T) results. In the case of YbH the deviation is more modest. There is no obvious difference in quality between the quasi-relativistic approach and the ZORA approach and the source of the overbinding is unclear. The ADF program estimates the energy error due to approximations in the computation of the exchange–correlation energy. This error is estimated to be negligible for the atoms and 1.3 kJ or less for the molecules. It is unlikely that the overbinding is due to the relativistic treatment since Hong et al. [38] recently reported excellent agreement between the scalar-relativistic formulation of the ZORA approach (with gauge invariance correction) and the DK–Hess approach for bond strengths and geometries of lanthanide and actinide diatomics. The lack of g functions in ADF probably has only a small effect, since employing the small-core basis set without g functions in Gaussian98 calculations reduced the bond strengths by only 2–4 kJ/mol. Baerends et al. [72] have pointed out that the commonly used density functionals for exchange–correlation are not invariant over the set of densities belonging to a degenerate ground state. This may lead to uncertainty of 10–20 kJ/mol in ground-state energies for main-group and transition elements provided that the correct symmetry is used (such as we do in these calculations). Uncertainties for *f* elements are not reported, but are most likely similar or slightly larger. Note that this uncertainty will cancel, at least to some extent, with respect to dissociation energies, particularly since the same *f* occupation is used in the atom and the molecule. We have not pursued the matter further, and it is not clear how these rather large systematic discrepancies arise.

Wang and Schwarz [34] reported quasi-relativistic bond strengths of YbH, YbF, and GdF (Table 4) obtained with the AMOL [73] program, which is the direct predecessor to ADF [49]. Their results agree well with the experimental results and much weaker bond strengths relative to our ADF results were obtained. Wang and Schwarz applied the VWN parameterization of the LDA [12] with Stoll's [56] local correlation correction and Becke's [11] gradient correction to the exchange energy. Their approach differs from ours by the local and gradient correction of the correlation energy, as well as the use of somewhat different basis sets. We used the same frozen-core level and (probably) the same quasi-relativistic approach.

Analysis of the chemical bond

There is general interest in the contribution of 4*f* to the chemical bonds. In our restricted open-shell HF (ROHF) orbitals for YbF the $4f_0$ orbital mixes (around 25%) with the $2p_0$ orbital of F. However, including 4*f* in the frozen core of Yb reduces the bond strength by only 7 kJ at the CCSD(T) level[2]. This confirms that the 4*f* orbitals do not behave as valence orbitals and contribute little to the chemical bond. The mixing is thus due to accidentally similar orbital energies.

The lanthanide 5*p* and the fluorine 2*s* mix strongly in all our LnF systems. The same effect is also reported for Dirac–HF calculations on GdF, by Tatewaki and Matsuoka [74], and for four-component DFT calculations by Dolg et al. [21]. Tatewaki and Matsuoka suggest that the mixing is due to a covalent chemical bond.

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[2] The orbitals are optimized in the separate atoms at the ROHF level, and are kept frozen when the atoms are brought to (experimental) molecular distances. Only the electrons in the relaxed orbitals are kept active in CCSD(T).

Table 5. Dissociation energies calculated with CCSD(T) at different levels of frozen atomic orbitals, D_e (kJ/mol). The orbitals are optimized in the separate atoms at the restricted open-shell HF level, and are kept frozen when the atoms are brought to (experimental) molecular distances. All the orbitals mentioned are relaxed and only the electrons in these orbitals are kept active in CCSD(T). Normal correlation means correlating the electrons in the orbitals 4*f*, 5*p*, 5–6*s* for Eu, Gd, and Yb, and 2*s* and 2*p* for F

	EuF	GdF	YbF
Ln 6*s*, F 2*p*	–	–	451
Ln 4*f*,6*s*, F 2*p*	504	589	458
Ln 4*f*,5*p*,5–6*s*, F 2*p*	512	616	–
Ln 4*f*,5*p*,5–6*s*, F 2*s*,2*p*	519	624	465
All orbitals relaxed + normal correlation	525	624	465

However, Dolg et al. [21] argue that this mixing is rather due to accidentally similar orbital energies, partly because including F 2*s* and Ln 5*s*–*p* in the frozen core decreases the binding energy by only 10 and 15 kJ, respectively. We included different sets of orbitals in the frozen core for EuF, GdF, and YbF, and the binding energies at the CCSD(T) level are presented in Table 5. When including the F 2*s* and the Ln 5*s*–5*p* in the frozen core, the binding energy of GdF decreases by 35 kJ. Including the same orbitals in EuF and YbF leads to a smaller decrease: 15 and 7 kJ, respectively. The small change in binding energy for YbF does, in particular, indicate that the mixing is due to orbital rotations rather than to covalent effects. The large effect (35 kJ) for GdF compared to that for EuF and YbF does not necessarily indicate covalent contribution to the bonding; it is more likely to be due to orbital polarization effects. The latter assumption is supported by the difference in electronic occupation. Gd has a $4f^7 5d^1 6s^2$ configuration, where the *d* electron is partly transferred to F upon bond formation. This will lead to a contraction of the 5*s* and 5*p*, which is prevented when these orbitals are included in the frozen core. Neither Eu nor Yb has any 5*d* electrons, and for these atoms a 6*s* rather than a 5*d* electron is transferred to F upon bond formation. This leads to a much smaller effect on the 5*s* and 5*p* orbitals since the 6*s* region overlaps the 5*s* and 5*p* region less than the 5*d* orbital. This is a probable cause for the larger effect for GdF than for EuF and YbF of freezing the F 2*s* and Ln 5*s*–5*p* orbitals.

The σ_{6s} orbital, calculated at the ROHF level, is polarized away from the negatively charged F and H atoms, leading to minimal orbital overlap F 2*p*. This indicates that the bond has prevailing ionic rather than covalent character. This is consistent with the findings of others [55, 75, 76].

Conclusions

Different DFT functionals have been evaluated by studying geometries and bond strengths of YbH, YbF, EuF, GdF, and NdF. Owing to the scarcity of accurate, undisputed experimental data on bond strengths, we have compared the DFT results both with available experimental data and with accurate CCSD(T) results. Our CCSD(T) results are in excellent agreement with available experimental data. The estimated BSSE is not large: 3 kJ or less for YbH and about 10 kJ for the LnF.

The DFT calculations with small-core RECPs generally give bond lengths a few picometers shorter than the large-core RECPs and are in very good agreement with the experimental results. The B3LYP and BP86 functionals give very similar geometries, while the results of BLYP calculations deviate slightly more from the experimental results. The calculated DFT bond strengths are also in good agreement with the CCSD(T) and experimental results. B3LYP always gives the smallest values and closest agreement, followed by BLYP and then the BP86 functional, which both also appear to give a good description of the bonding. There are surprisingly small differences between the bond strengths calculated with large-core and small-core RECPs, since large-core RECPs have been shown to be less accurate in earlier studies [70, 75, 77]. The use of small-core RECPs is significantly more resource demanding, partly owing to an extensive basis set, compared to the small-core RECPs, and the results presented here rather support than exclude the use of the large-core RECPs unless very accurate calculations are required. However, the large-core RECPs should be used with care and tested (if feasible) whenever used.

The ADF calculations systematically overbind the fluorides more than any other approach we have used. The reason for this is unclear, and appears to be due neither to the relativistic treatments nor to the applied functionals.

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