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# Lanthanide Diatomics and Lanthanide Contractions

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Density functional (DF) calculations including gradient-exchange and correlation corrections have been performed on the LnH, LnO, and LnF series (Ln = La, Gd, Yb, and Lu). Relativistic first-order perturbations including S–O couplings are accounted for. The calculated molecular constants are in reasonable agreement with the experimental ones. The calculated lanthanide contractions of the three series, i.e.  $R(\text{La}-\text{X}) - R(\text{Lu}-\text{X})$ , are quite different, 0.19 Å (0.19 Å) for LnH, 0.10 Å (0.11 Å) for LnF, and only 0.05 Å (0.04 Å) for LnO. There is good agreement between the calculated values and the experimental ones (values in parentheses). This astonishing variation has two origins, a monoatomic and a diatomic one, which are related to each other. The first point is the noninteger 4f-shell population. Participation of unoccupied 4f-AOs in outer-valence shell bonding is important for strongly bound lighter lanthanides. The second point is the “rigidity” of the bond: the larger the bond energy or the force constant, the smaller the lanthanide contraction.

## 1. Introduction

Lanthanide chemistry has become the subject of attention in many areas.<sup>1–4</sup> The 15 elements from La ( $Z = 57$ ,  $N = 0$ ) to Lu ( $Z = 71$ ,  $N = 14$ ) are characterized by gradual filling of the 4f subshell. The radial density of the 4f shell is well inside of the 5s–5p core, but its energy is much higher. So the “inner valence” 4f shell is called an “open core” shell. Because of the high angular momentum and spin multiplicity of the low-lying electronic states of the Ln atoms with partially filled 4f, 5d, 6s orbitals, a large number of low-lying molecular electronic states result, which are split by spin–orbit coupling.

A simple model for the electronic structure of lanthanide diatomics developed by Field<sup>5</sup> has proven to be a useful tool for the interpretation of their electronic spectra. According to this approach, a formal charge is assigned to the lanthanide atom, and then all configurations arising from a general Ln 4f<sup>*n*</sup> configuration, combined with a specific outer-valence configuration, are treated as one so-called superconfiguration. The electronic states belonging to the same superconfiguration have almost the same rotational and vibrational constants, independent of the specific electronic coupling within the 4f subshell and between the 4f subshell and the valence subconfiguration. This model has been successfully applied in the ligand field approach<sup>6,7</sup> and in pseudopotential<sup>8–11</sup> and density functional calculations.<sup>12</sup>

In this paper, we want to apply the superconfiguration model in the density functional approach to the rare earth monohydrides LnH, monofluorides LnF, and monoxides LnO. Four lanthanides are chosen: La, Gd, Yb, and Lu. The reason for this choice is that La, Gd, and Lu have a (nearly) empty, half-filled and full 4f<sup>*N*</sup> shell, respectively, in their compounds. Yb is an interesting lanthanide because of the nearly degenerate 4f<sup>*N*</sup> and 4f<sup>*N*+1</sup> ground configurations in some compounds (e.g., YbO).

It is well-known that quantum chemical calculations on molecules containing heavy atoms, especially the lanthanides with open d and f shells, have to account for large correlation and relativistic effects. Present day *ab initio* methods have already severe problems with the 3d 4s 4p shells of the first transition elements.<sup>13</sup> So, in the present work, we use a cheap approximation scheme, the density functional approach including correlation corrections, nonlocal gradient exchange corrections, and relativistic first-order perturbation corrections.

The calculated molecular constants are in reasonable agreement with the experimental data. We find the lanthanide contractions to be different for these three molecular series. From La to Lu, the bond contractions are (experimental values in parentheses) 0.19 Å (0.19 Å) for LnH, 0.10 Å (0.11 Å) for LnF, and only 0.05 Å (0.04 Å) for LnO.

An important aspect of lanthanide chemistry is the variable 4f-AO population. Since the 4f-AOs are localized inside the atomic core and overlap only weakly with ligand orbitals, they result only in weak covalent interactions. Nevertheless, the 4f population may strongly deviate from integer values<sup>12,14</sup> because of some mixing of unoccupied 4f-AOs into the occupied *outer-valence* MOs. This is so even in the superconfiguration model where the *inner-valence* 4f-type MOs have been occupied by an integer number of electrons. Thereby the effective charge of the ionic core of the lanthanide, and the electronic structure and bonding properties of the outer-valence shell, and also the effective radius of Ln are modified. Another point is that the variability of the lanthanide radii depends on the strength of the bond to the ligand. The more rigid the bond, i.e., the larger force constant or bond energy, the smaller the lanthanide contraction.

The paper is organized as follows. Computational details are given in section 2. In section 3, the results are presented and discussed. The calculated molecular constants are compared with the available experimental data. Mulliken populations are analyzed, and on the basis of bond energy decompositions one achieves an understanding of the bonding mechanism in these lanthanide compounds. The lanthanide contractions are discussed in section 4. The results are summarized in section 5.

## 2. Computational Details

The Amsterdam Density-Functional (DF) Program Package AMOL<sup>15–17</sup> has been used.

The frozen core approximation is adopted for F (1s<sup>2</sup>), O (1s<sup>2</sup>), and for Ln (1s<sup>2</sup> ... 4p<sup>6</sup>4d<sup>10</sup>). According to the superconfiguration model, the 4f shell is evenly occupied by an integer number of electrons (see below). However, the inner-valence 4f shell is not frozen but allowed to relax upon bond formation in the outer-valence shell. Furthermore, 4f basis functions are allowed to contribute to the outer-valence MOs. Because of variable inner screening by variably populated 4f functions, the 5s–5p shells are also unfrozen. The 5s–5p shell is so stable that it remains

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, June 15, 1995.

**TABLE 1: Slater Orbital Exponents of La, Gd, Yb, Lu, H, O, and F**

orbital	La	Gd	Yb	Lu	H	O	F
1s	38.50	37.95	41.10	42.85	1.58 0.92 0.69	7.36	8.33
2s	20.70	22.75	27.80	27.70		7.58 2.88 1.72	3.24 1.94 0.74
2p	25.35	28.81	31.78	32.28	1.25 0.80	4.08 2.08 1.12	4.54 2.30 1.24
3s	13.10	16.15	15.90	16.30			
3p	12.62	14.68	16.43	16.72			
3d	15.00	17.55	18.85	19.55		3.10 1.60	3.40 1.75
4s	7.60	8.50	10.25	10.45			
4p	6.59	7.75	8.68	8.84			
4d	6.80	8.20	9.70	9.75			
4f	8.35	10.40	11.80	12.00			
	4.00	5.15	5.80	5.90			
	1.85	2.40	2.65	2.70			
5s	3.95	4.55	5.00	5.00			
	3.28	3.65	3.90	4.10			
	2.60	2.95	3.20	3.20			
5p	3.55	4.00	4.40	4.45			
	2.88	3.25	3.35	3.55			
	2.20	2.45	2.65	2.65			
5d	2.85	3.25	3.45	3.50			
	1.65	1.75	1.80	1.75			
	0.95	0.95	0.95	0.90			
6s	1.85	2.10	2.20	2.25			
	1.20	1.40	1.40	1.45			
	0.80	0.90	0.90	0.95			
6p	1.53	1.55	1.50	1.75			
	1.00	0.70	0.80	0.85			

fully occupied and does not take part in bonding, but its radius is important for the bond lengths because of the Pauli repulsion.

The valence shells are expanded in triple-zeta STOs which have been optimized by Baerends et al.,<sup>18,19</sup> and double-zeta polarization functions are added (H 2p, O 3d, F 3d, Ln 6p); see Table 1. Density functional SCF-polarization of Ln 4f by 5g turns out to be small and is neglected further on.

Two kinds of DF approximations<sup>20–23</sup> are used. The standard HFS method including the correlation correction due to Vosko et al.<sup>24</sup> and Stoll et al.<sup>25</sup> is labeled as C. F (full correction) indicates that Becke's<sup>26</sup> gradient correction for the exchange potential is added to the C approach. The relativistic corrections in the valence shell are accounted for by the first-order Pauli perturbation approach comprising mass-velocity (MV), Darwin (DW), spin-orbit (SO), and so-called indirect core effects (DVC). The cores are treated at the Dirac–Fock–Slater level.

LnH, LnF, and LnO have been calculated in their ground configurations. In general, the lanthanides are trivalent;<sup>27</sup> i.e., the valence configuration is  $f^N$  with  $N = 0, 7$ , and 14 for La, Gd, and Lu, respectively. But for Yb ( $N = 13$ ) also the divalent state is common, with occupied  $f^{N+1}=14$  shell. The superconfigurations of the ground states in general are:  $(4f^N)\sigma^2\sigma^2$  for LnH,  $(4f^N)\sigma^2\sigma^2\sigma^2\pi^4$  for LnF and  $(4f^N)\sigma^2\sigma^2\sigma^1\pi^4$  for LnO. However, there are exceptions. Concerning the Yb compounds, the ground configurations are  $(4f^{14})\sigma^2\sigma^1$  for YbH,  $(4f^{14})\sigma^2\sigma^2\sigma^1\pi^4$  for YbF, and  $(4f^{14})\sigma^2\sigma^2\sigma^2\pi^4$  for YbO. The significant  $(4f^{13})\sigma^2\sigma^2\sigma^1\pi^4\ ^1\Sigma^+$  admixture in the YbO ground state<sup>12</sup> has been neglected here except where explicitly noted. Another exception is LaH:  $4f^0\sigma^2\sigma^2$  represents one of the low-lying excited states.

### 3. Calculational Results and Discussion

The calculated molecular spectroscopic constants of LnH, LnF, and LnO and the available experimental data<sup>28–38</sup> are

summarized in Table 2, (a) (LnH), (b) (LnF), and (c) (LnO), and are compared with calculated values from the literature.

**3.1. Bond Lengths.** The calculated bond lengths are in reasonable agreement with the experimental data, within a few picometers. At the DF(C) level, the calculated bond lengths are usually smaller than the experimental ones for light atomic systems,<sup>42,43</sup> while the DF(F) results are usually too long. Also for the lanthanide compounds, Becke's correction expands the bond lengths by several picometers. The calculated bond lengths tend to be too short for LnH, so the DF(F) results are a little better than the DF(C) ones. For LnO and LnF, the calculated bond lengths tend to be too large, and the DF(C) results are slightly better on the average. Relativistic contractions of these bond lengths are not large, only about  $-0.00$  to  $-0.03$  Å, except for GdF ( $-0.06$  Å). Dolg and Stoll,<sup>40</sup> on the contrary, found slight bond length expansions up to  $+0.02$  Å.

**3.2. Bond Energies.** The determination of dissociation energies ( $D_e$  taken with positive sign) is a difficult problem for theoretical approaches. Typical deviations between experimental data and theoretical results at the *ab initio* MP2 or CISD levels are about  $-1$  eV<sup>42,43</sup> for light molecules. The dissociation energies are often underestimated by Slater's simple  $X\alpha$ -DF method, on the average by  $-1$  eV; the DF(C) increases  $D_e$  significantly, on the average by  $+1.5$  eV, and Becke's correction DDF(F) reduces the average error for light systems to a few tenths of an electronvolt.<sup>42,43</sup>

For heavy systems, the correlation correction does not work so well. This has already been pointed out by Lagowski and Vosko<sup>13</sup> for the 3d shell. For the lanthanide compounds, which contain open 4f and 5d shells, the standard DF correlation corrections also cannot completely overcome the correlation error.<sup>12</sup> In this paper, we restrict our interest to the ground states of molecules, where the 4f shell occupancy does not change from free atoms to molecules. So, the correlation error of  $D_e$  remains reasonably small, and we have omitted here the empirical correlation corrections of ref 12.

Relativity reduces the bond energies, depending on the molecules, by 0–3 eV; see section 3.5. There exists no simple rule connecting the small relativistic bond length contractions and the sometimes large bond energy reductions. Gordy's rule,<sup>44</sup> namely that bond length contraction should be accompanied by bond energy increase, does not even qualitatively apply to relativistic changes.

Relativity improves the  $D_e$  values drastically. The average absolute deviations of the present  $D_e$  are 0.5 eV for DF(C) and 0.4 eV for DF(F).

**3.3. Vibrational Frequencies.** For light molecules, the mean absolute deviation of *ab initio* MP2 or CI vibrational frequencies is typically about  $100\text{ cm}^{-1}$ , that of simple DF is about  $70\text{ cm}^{-1}$ , and that corrected DF(C) and DF(F) is about  $50\text{ cm}^{-1}$ .<sup>43</sup> In the present work, the deviation of the DF(F) is about  $40\text{ cm}^{-1}$  and of the DF(C) is about  $30\text{ cm}^{-1}$ . The DF(C) and the higher level DF(F) are not very different for frequency calculations in the cases of both light and heavy molecular systems.

According to Badger's rule,<sup>45</sup> the vibrational frequency changes in a series of similar molecules should be negatively proportional to the respective bond length changes. In our calculations, the bond lengths are weakly shortened by relativistic corrections. The frequencies in general increase for LaF, GdF, and GdO, by as much as  $100$ – $130\text{ cm}^{-1}$ . However, there is obviously no proportionality between frequency increases and bond length contractions. That is, Badger's rule is not applicable to relativistic changes.

**TABLE 2: Calculated Bond Distances  $R_e$  (in Å), Dissociation Energies  $D_e$  (in eV), and Vibrational Frequencies  $\omega_e$  (in  $\text{cm}^{-1}$ ) of (a) LaH( $f^0\sigma^2\ ^1\Sigma$ ), GdH( $f^7\sigma^2\ ^8\Sigma$ ), YbH( $f^{14}\sigma^1\ ^2\Sigma$ ), and LuH( $f^{14}\sigma^2\ ^1\Sigma^+$ ) Using Different DF Approaches,<sup>a</sup> (b) for LaF( $f^0\sigma^2\ ^1\Sigma$ ), GdF( $f^7\sigma^2\ ^8\Sigma$ ), YbF( $f^{14}\sigma^1\ ^2\Sigma$ ), and LuF( $f^{14}\sigma^2\ ^1\Sigma$ ), and (c) for LaO( $f^0\sigma^2\ ^2\Sigma$ ), GdO( $f^7\sigma^1\ ^9\Sigma$ ), YbO( $f^{14}\sigma^0\ ^1\Sigma$ ), and LuO( $f^{14}\sigma^1\ ^2\Sigma$ )**

(a) LaH, GdH, YbH, and LuH									
	LaH	GdH	YbH	LuH		LaH	GdH	YbH	LuH
$R_e(\text{exp})$	2.10 <sup>b</sup>		2.05	1.91	$D_e^{\text{nr}}(\text{C})$	3.08	2.77	1.96	3.21
$R_e^{\text{r}}(\text{F})$	2.08	1.99	2.08	1.89	$D_e^{\text{r}}(\text{PPCI})$	2.71	2.52	1.57	3.24
$R_e^{\text{r}}(\text{C})$	2.05	1.97	2.05	1.87	$D_e^{\text{r}}(\text{PPCI}^*)$	3.01			3.47
$R_e^{\text{nr}}(\text{F})$	2.11	2.01	2.11	1.92	$\omega_e(\text{exp})$			1249	1520
$R_e^{\text{nr}}(\text{C})$	2.07	1.98	2.06	1.89	$\omega_e^{\text{r}}(\text{F})$	1378	1507	1193	1567
$R_e^{\text{r}}(\text{DHF-OCE})$	2.22			2.01	$\omega_e^{\text{r}}(\text{C})$	1415	1535	1236	1572
$R_e^{\text{r}}(\text{PPCI})$	2.09	1.99	2.09	1.95	$\omega_e^{\text{nr}}(\text{F})$	1347	1461	1182	1506
$R_e^{\text{r}}(\text{PPCI}^*)$	2.01			1.94	$\omega_e^{\text{r}}(\text{C})$	1397	1490	1236	1524
$D_e(\text{exp})$			≤1.63	3.47	$\omega_e^{\text{r}}(\text{DHF-OCE})$	1402			1557
$D_e^{\text{r}}(\text{F})$	2.99	2.67	1.58	3.20	$\omega_e^{\text{r}}(\text{PPCI})$	1450	1471	1282	1445
$D_e^{\text{r}}(\text{C})$	2.96	2.63	1.56	3.18	$\omega_e^{\text{r}}(\text{PPCI}^*)$	1461			1493
$D_e^{\text{nr}}(\text{F})$	3.11	2.81	1.98	3.23					
(b) LaF( $f^0\sigma^2\ ^1\Sigma$ ), GdF( $f^7\sigma^2\ ^8\Sigma$ ), YbF( $f^{14}\sigma^1\ ^2\Sigma$ ), and LuF( $f^{14}\sigma^2\ ^1\Sigma$ ) <sup>c</sup>									
	LaF	GdF	YbF	LuF		LaF	GdF	YbF	LuF
$R_e(\text{exp})$	2.03	1.97	2.02	1.92	$D_e^{\text{nr}}(\text{C})$	8.25	8.00	6.41	7.98
$R_e^{\text{r}}(\text{F})$	2.07	1.96	2.07	1.95	$D_e^{\text{r}}(\text{PPCI})$	6.02	5.73	4.99	7.04
$R_e^{\text{nr}}(\text{F})$	2.10	2.03	2.08	1.96	$D_e^{\text{r}}(\text{PPCI}^*)$	6.55			7.28
$R_e^{\text{r}}(\text{C})$	2.03	1.89	1.99	1.89	$\omega_e(\text{exp})$	570	611	506	612
$R_e^{\text{nr}}(\text{C})$	2.05	1.95	2.01	1.90	$\omega_e^{\text{r}}(\text{F})$	594	613	489	586
$R_e^{\text{r}}(\text{PPCI})$	2.12	2.08	2.05	1.94	$\omega_e^{\text{r}}(\text{C})$	653	692	530	661
$R_e^{\text{r}}(\text{PPCI}^*)$	2.02			1.93	$\omega_e^{\text{nr}}(\text{F})$	476	502	477	586
$D_e(\text{exp})$	6.24	6.12	4.83	5.94 <sup>d</sup>	$\omega_e^{\text{nr}}(\text{C})$	548	587	530	656
$D_e^{\text{r}}(\text{F})$	6.38	5.85	5.18	7.26	$\omega_e^{\text{r}}(\text{PPCI})$	571	548	495	598
$D_e^{\text{r}}(\text{C})$	7.08	6.73	5.88	8.08	$\omega_e^{\text{r}}(\text{PPCI}^*)$	582			599
$D_e^{\text{nr}}(\text{F})$	7.62	7.21	5.73	7.17					
(c) LaO( $f^0\sigma^1\ ^2\Sigma$ ), GdO( $f^7\sigma^1\ ^9\Sigma$ ), YbO( $f^{14}\sigma^0\ ^1\Sigma$ ), and LuO( $f^{14}\sigma^1\ ^2\Sigma$ )									
	LaO	GdO	YbO	LuO		LaO	GdO	YbO	LuO
$R_e(\text{exp})$	1.83	1.81	1.85 <sup>e</sup>	1.79	$D_e^{\text{nr}}(\text{C})$	10.01	10.73	5.89	8.92
$R_e^{\text{r}}(\text{F})$	1.89	1.82	1.90 <sup>e</sup>	1.83	$D_e^{\text{r}}(\text{PPCI})$	6.42	5.78	3.22	6.12
$R_e^{\text{r}}(\text{C})$	1.84	1.77	1.87	1.79	$D_e^{\text{r}}(\text{PPCI}^*)$	8.02			6.49
$R_e^{\text{nr}}(\text{F})$	1.89	1.86	1.94	1.83	$\omega_e(\text{exp})$	813	824	699 <sup>e</sup>	842
$R_e^{\text{nr}}(\text{C})$	1.84	1.80	1.88	1.79	$\omega_e^{\text{r}}(\text{F})$	761	810	680 <sup>e</sup>	796
$R_e^{\text{r}}(\text{PPCI})$	1.95	1.91	1.81	1.80	$\omega_e^{\text{r}}(\text{C})$	814	878	678	857
$R_e^{\text{r}}(\text{PPCI}^*)$	1.81			1.79	$\omega_e^{\text{nr}}(\text{F})$	699	684	623	800
$D_e(\text{exp})$	8.28	7.44	4.12 <sup>e</sup>	7.04	$\omega_e^{\text{nr}}(\text{C})$	762	764	687	853
$D_e^{\text{r}}(\text{F})$	7.60	6.68	4.13 <sup>e</sup>	6.94	$\omega_e^{\text{r}}(\text{PPCI})$	829	780	849	852
$D_e^{\text{r}}(\text{C})$	8.77	7.90	5.04	8.08	$\omega_e^{\text{r}}(\text{PPCI}^*)$	847			861
$D_e^{\text{nr}}(\text{F})$	8.82	9.60	4.91	7.79					

<sup>a</sup> C, correlation correction; F, full DF with correlation and exchange-gradient corrections. The superscripts nr and r denote the nonrelativistic and relativistic results, respectively. exp = experimental data.<sup>31-41</sup> DHF-OCE: Dirac-Hartree-Fock one-center expansion from Pyykkö.<sup>14</sup> PPCI: pseudopotential CI with frozen 4f shell from Dolg et al.<sup>10,39,40</sup> \*: variable 4f occupation is allowed for.<sup>40,41</sup> <sup>b</sup> It is not unequivocal, whether this  $^1\Sigma$  value refers to the  $f^0\sigma^2\sigma^2$  configuration. <sup>c</sup> Experimental data, see ref 56. <sup>d</sup> Seems to be questionable. <sup>e</sup>  $f^{14}/f^{13}\sigma^1$  mixed state.<sup>12,59</sup>

**3.4. Mulliken Populations and Dipole Moments.** Mulliken populations of DF(F) SCF wave functions are presented in Table 3, a, b, and c. In the neutral atoms, 6s is doubly occupied, while 4f and 5d compete for electrons, resulting in  $5d^1$  for La, Gd, and Lu but  $5d^0$  for Yb. The 6s population decreases upon bond formation, by about  $1/2$  e in the case of monovalent ligands (H, F) and by more than 1 e in the case of divalent O. In  $\text{Ln}^{2+}$  bonded to electronegative atoms, 4f is less screened than in  $\text{Ln}^0$  and thereby is stabilized. Accordingly, the f-shell population is increased by about  $1/3$  to  $1/2$  e upon bonding to an electronegative ligand (O, F). Fractionally increased 4f population, of course, does not occur for Yb and Lu, which have already a full 4f shell.

The atomic Mulliken charges on the lanthanides are about +0.3 to +0.6 for  $\text{LnH}$ , +0.4 to +0.7 for  $\text{LnF}$ , and +0.6 to +0.8 for  $\text{LnO}$ , corresponding to the negative dipole moments. We note that the dipole moments of the fluorides are not larger than those of the hydrides, while those of the oxides are significantly

larger. Because of the large atomic contributions from the diffuse Ln 6s6p5d outer-valence shell hybrids (see also refs 59 and 63) to the molecular dipole moment, there is no direct relation between  $\mu$  and the ionicity of the bond, or the charge values in the point charge model. The Yb compounds are more polar both on the basis of dipole moments and Mulliken charges. We note that Dolg et al. found very different dipole moments when treating the 4f shell as a frozen core shell, see for instance GdF in Table 3b.

**3.5. Analysis of Nonrelativistic and Relativistic Contributions to the Bond Energy.** The bond energy is the difference of the relativistic energies  $E^{\text{r}}$  between atoms and molecule:

$$D_e^{\text{r}} = (E_{\text{A}}^{\text{r}} + E_{\text{B}}^{\text{r}}) - E_{\text{AB}}^{\text{r}}$$

It also can be evaluated from its nonrelativistic value  $D^{\text{nr}}$  and the relativistic correction  $\delta^{\text{r}}D$ , which both can be broken down

**TABLE 3: Mulliken Populations of (a) LnH, (b) LnF, and (c) LnO at the Nonrelativistic DF(F) Level and Relativistic Dipole Moments<sup>a</sup>**

(a) LnH				
	LaH	GdH	YbH	LuH
Ln				
4f	0.00	7.00	14.00	14.00
5d	1.10	1.04	0.32	0.91
6s	1.28	1.70	1.02	1.83
6p	0.00	0.00	0.12	0.01
H				
1s	1.60	1.23	1.51	1.20
2p	0.02	0.03	0.03	0.05
$Q_{Ln}$	0.62	0.26	0.54	0.25
$-\mu$	2.82	2.38	3.12	1.90
$-\mu(\text{PPCI})$	2.86	2.16	2.81	1.58
(b) LnF				
	LaF	GdF	YbF	LuF
Ln				
4f	0.42	7.42	14.00	14.01
5d	0.71	0.35	0.32	0.57
6s	1.14	1.81	0.86	1.77
6p	0.05	0.00	0.09	0.00
F				
2s	2.16	2.06	2.08	2.08
2p	5.51	5.35	5.65	5.57
3d	0.01	0.01	0.00	0.00
$Q_{Ln}$	0.68	0.42	0.73	0.65
$-\mu$	2.18	1.18	3.64	2.11
$-\mu(\text{PPCI})$	2.07	6~7 <sup>b</sup>	3.56	2.07
(c) LnO				
	LaO	GdO	YbO	LuO
Ln				
4f	0.36	7.76	13.98	14.01
5d	1.12	0.76	0.93	1.25
6s	0.82	0.86	0.09	0.85
6p	0.16	0.05	0.17	0.15
O				
2s	1.93	1.97	1.94	1.95
2p	4.59	4.58	4.88	4.78
3d	0.02	0.02	0.01	0.01
$Q_{Ln}$	0.54	0.57	0.83	0.74
$-\mu$	3.73	2.90	7.60	4.58
$-\mu(\text{PPCI})$	3.96	4.25 <sup>c</sup>	8.05	5.57

<sup>a</sup>  $Q$ : atomic charge.  $\mu$ : dipole moment in debyes. PPCI: pseudo-potential CI from Dolg et al.<sup>10,39,40</sup> <sup>b</sup> Nonrelativistic value. <sup>c</sup> Nonrelativistic result with small basis set.

into several parts  $\Delta^{\text{nr}}$  and  $\Delta\delta^{\text{r}}$ ,<sup>17,46</sup> see the legend of Table 4:

$$D_e^{\text{r}} = D^{\text{nr}} + \delta^{\text{r}}D$$

$$= (\Delta_{\text{EA}}^{\text{nr}} + \Delta_{\text{PR}}^{\text{nr}} + \Delta_{\text{INT}}^{\text{nr}}) +$$

$$(\Delta\delta_{\text{MV}}^{\text{r}} + \Delta\delta_{\text{DW}}^{\text{r}} + \Delta\delta_{\text{DVC}}^{\text{r}} + \Delta\delta_{\text{SO}}^{\text{r}}) \quad (1)$$

Concerning the bond energy decomposition, La, Gd, and Lu show much similarity. In all three molecular series the atomic electrostatic attraction  $\Delta_{\text{EA}}^{\text{nr}}$  is smaller for Yb, because the latter atom does not have a 5d electron to be attracted by the ligand's core upon overlapping of the charge clouds. Conversely, the Pauli repulsion between the atomic shells is significantly smaller for Yb which has  $N + 1$  f electrons, because the inner 4f shell does not contribute very much to the overlap. Also the quantum mechanical stabilizing orbital interaction is smaller in the Yb compounds. As a consequence, the nonrelativistic bond energies of the Yb compounds are about 20–40% smaller than those of their Ln analogues.

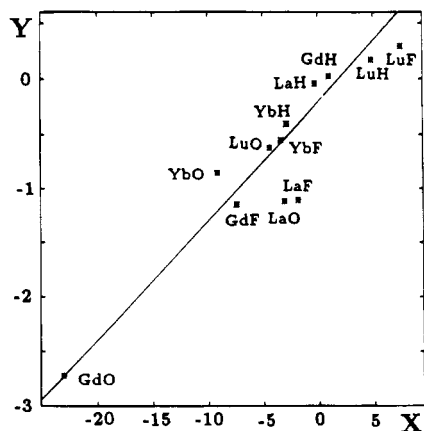
Relativity in general destabilizes these bonds, which can be roughly explained by reduced Ln 6s population (6s is relativ-

**TABLE 4: Bond Energy Decomposition of (a) LnH, (b) LnF, and (c) LnO (Ln = La, Gd, Yb, Lu) at the DF(F) Level<sup>a</sup>**

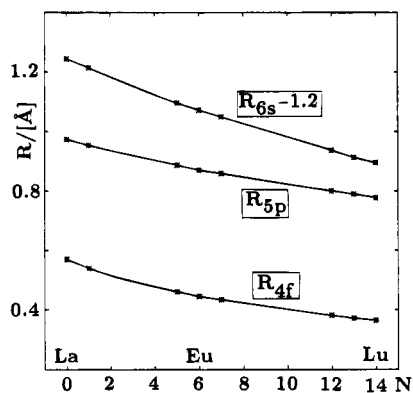
(a) LnH				
	LaH	GdH	YbH	LuH
$\Delta_{\text{EA}}^{\text{nr}}$	1.33	1.45	1.02	1.67
$\Delta_{\text{PR}}^{\text{nr}}$	-5.43	-5.54	-3.15	-6.19
$\Delta_{\text{PRO}}^{\text{nr}}$	-4.31	-4.31	-2.36	-4.76
$\Delta_{\text{INT}}^{\text{nr}}$	7.42	7.12	4.34	7.99
$D^{\text{nr}}$	3.11	2.81	1.98	3.23
$\Delta\delta_{\text{MV}}^{\text{r}}$	-0.13	-0.06	-1.20	0.18
$\Delta\delta_{\text{DW}}^{\text{r}}$	0.10	0.09	0.78	0.02
$\Delta\delta_{\text{DVC}}^{\text{r}}$	-0.01	-0.01	0.02	-0.03
$\Delta\delta_{\text{SO}}^{\text{r}}$	-0.09	-0.17	-0.00	-0.21
$\delta^{\text{r}}D$	-0.12	-0.14	-0.40	-0.04
$D_e^{\text{r}}$	2.99	2.67	1.58	3.19
(b) LnF				
	LaF	GdF	YbF	LuF
$\Delta_{\text{EA}}^{\text{nr}}$	3.33	3.98	2.46	3.76
$\Delta_{\text{PR}}^{\text{nr}}$	-10.61	-12.38	-4.63	-11.25
$\Delta_{\text{PRO}}^{\text{nr}}$	-7.84	-9.00	-2.77	-8.06
$\Delta_{\text{INT}}^{\text{nr}}$	15.43	16.17	8.50	15.23
$D^{\text{nr}}$	7.59	7.17	5.73	7.17
$\Delta\delta_{\text{MV}}^{\text{r}}$	-0.69	-1.44	-1.66	0.40
$\Delta\delta_{\text{DW}}^{\text{r}}$	0.44	0.63	1.09	-0.08
$\Delta\delta_{\text{DVC}}^{\text{r}}$	-0.85	-0.34	0.03	-0.03
$\Delta\delta_{\text{SO}}^{\text{r}}$	-0.11	-0.17	-0.00	-0.21
$\delta^{\text{r}}D$	-1.21	-1.32	-0.55	0.09
$D_e^{\text{r}}$	6.38	5.85	5.18	7.26
(c) LnO				
	LaO	GdO	YbO	LuO
$\Delta_{\text{EA}}^{\text{nr}}$	5.89	6.53	4.01	5.79
$\Delta_{\text{PR}}^{\text{nr}}$	-19.71	-21.65	-8.70	-18.10
$\Delta_{\text{PRO}}^{\text{nr}}$	-14.56	-15.86	-5.45	-13.02
$\Delta_{\text{INT}}^{\text{nr}}$	23.38	25.44	10.36	20.81
$D^{\text{nr}}$	8.82	9.58	4.91	7.79
$\Delta\delta_{\text{MV}}^{\text{r}}$	-1.01	-4.08	-2.45	-1.83
$\Delta\delta_{\text{DW}}^{\text{r}}$	0.69	1.90	1.51	1.20
$\Delta\delta_{\text{DVC}}^{\text{r}}$	-0.80	-0.55	0.08	0.01
$\Delta\delta_{\text{SO}}^{\text{r}}$	-0.11	-0.17	-0.00	-0.23
$\delta^{\text{r}}D$	-1.23	-2.72	-0.86	-0.85
$D_e^{\text{r}}$	7.60	6.68	4.06	6.94

<sup>a</sup> The nonrelativistic bond energy  $D^{\text{nr}}$  consists of three contributions:  $\Delta_{\text{EA}}^{\text{nr}}$  (classical electrostatic attraction of unperturbed overlapping atoms),  $\Delta_{\text{PR}}^{\text{nr}}$  (quantum mechanical Pauli repulsion of orthogonalized atomic shells), and  $\Delta_{\text{INT}}^{\text{nr}}$  (quantum mechanical orbital interference and polarization).  $\Delta_{\text{EA}}^{\text{nr}} + \Delta_{\text{PR}}^{\text{nr}}$  is the "promolecule" energy  $\Delta_{\text{PRO}}^{\text{nr}}$ . The total relativistic bond energy correction  $\delta^{\text{r}}D$  contains contributions from the mass-velocity variation ( $\Delta\delta_{\text{MV}}^{\text{r}}$ ), the Darwin potential ( $\Delta\delta_{\text{DW}}^{\text{r}}$ ), the relativistic change of the core electrons' repulsion potential ( $\Delta\delta_{\text{DVC}}^{\text{r}}$ ), and the spin-orbit coupling ( $\Delta\delta_{\text{SO}}^{\text{r}}$ ).

istically stabilized) and by increased Ln 4f population in the molecules as compared to the free atoms (4f is destabilized). The extreme relativistic destabilization of GdO due to the velocity-mass effect (see Table 4c) is remarkable, yet. We note that the direct relativistic effects originate in the vicinity of the nucleus.<sup>47,48</sup> There is a linear relation between the change of electron charge in the spatial K-shell upon bond formation times  $Z^4$  and relativistic corrections to the bond energy.<sup>48</sup> This relation also holds for the lanthanide molecules, as shown in Figure 1. So we have traced back the large relativistic destabilization of GdO to the large decrease of electronic charge in the K shell of Gd upon formation of GdO from the atoms. We have also found in other cases<sup>47</sup> no good correlation between the "K-shell density" and Mulliken populations.



**Figure 1.** Correlation between  $X$  = electronic charge in the spatial region of the K-shell times  $Z^4$  ( $Z$  = nuclear charge) in units of  $10^2 e$ , and  $Y$  = relativistic correction to the bond energy in eV.



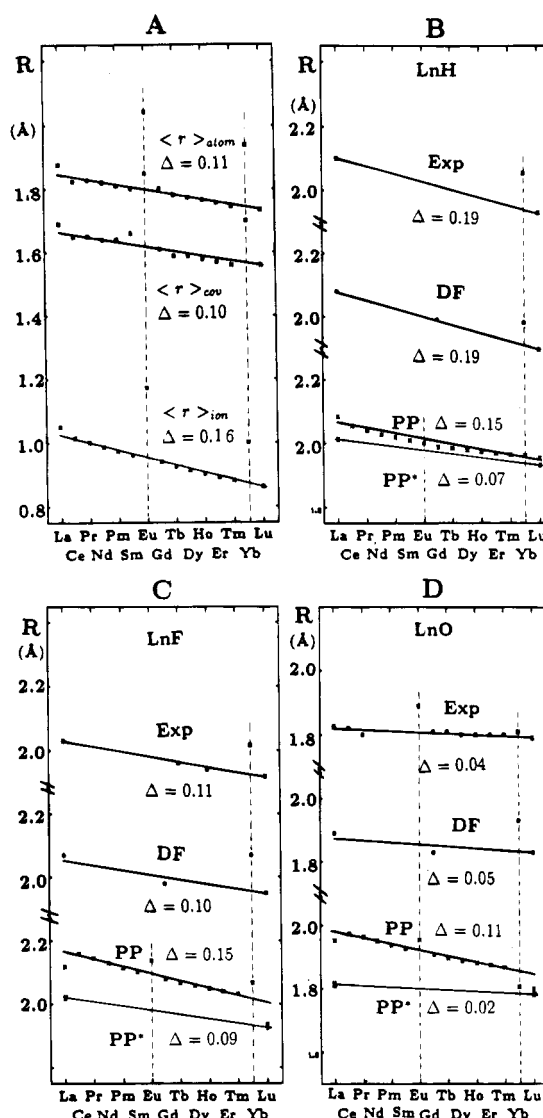
**Figure 2.**  $\langle r \rangle$  expectation values of 4f, 5p, and 6s AO of  $\text{Ln } 4f^N 5s^2 5p^6 5d^1 6s^2$  versus atomic number  $Z = 57 + N$ .

#### 4. Lanthanide Contraction

Covalent and ionic radii decrease upon moving from left to right in the periodic table because of the increase of the nuclear charge, and because each additional valence electron incompletely shields the extra nuclear charge. Due to the different orbital penetrations (see, e.g. Figure 1 of ref 12), the shielding strength of orbitals decreases in the order  $s > p > d > f$ . Therefore, there is a significant atomic contraction when the 4f shell is filled with 14 electrons through the lanthanide series of elements, which is known as the lanthanide contraction. It is stated in textbooks, for example, ref 27, that this contracts covalent and ionic bonds by about 0.2 Å.

**4.1. Atomic Radii.** Expectation values  $\langle r \rangle$  of lanthanide atomic orbitals from density functional calculations are plotted in Figure 2. The overall contractions from La to Lu are smaller for the inner atomic orbitals and larger for the outer ones. The contractions of the core-type orbitals 4f, 5s, and 5p are about 0.2 Å, and that of the 6s valence orbitals is more than 0.4 Å (only 0.35 Å at the nonrelativistic level), in agreement with literature values (see ref 40). As an exception, the 5d contraction is only 0.1 Å. Accordingly, one may expect diverse lanthanide contractions, depending on which Ln orbitals participate in the bonding of the respective molecular series.

The so-called experimental atomic radii are determined by a (somewhat arbitrary) splitting up of the experimental internuclear distances. These atomic radii depend on several factors, as the kind of bonding (ionic, covalent, van der Waals), valency number (2 or 3), coordination number, and valence electron configuration (high spin or low spin;  $f^{N-m-n} d^m s^n$ ).<sup>49</sup> The radii (atomic, covalent, and ionic) from *The Elements* by Emsley<sup>50</sup> and from the *Handbook of Rare Earths*<sup>51</sup> are plotted in Figure



**Figure 3.** Lanthanide contractions of atomic radii (in Å).  $\Delta$  is the mean contraction from La to Lu. (A) Experimental atomic radii,<sup>50</sup> atomic covalent radii,<sup>50</sup> and ionic radii<sup>51</sup> of lanthanide elements, (B)  $\text{LnH}$ , (C)  $\text{LnF}$ , (D)  $\text{LnO}$ : experimental and calculated bond lengths of  $\text{LnX}$  molecules. Exp, experimental; DF, present density functional results; PP: pseudopotential CI results of Dolg et al.<sup>39,52,54</sup> for frozen integer 4f<sup>N</sup>-population; PP\*: the same but with optimized 4f-valence shell.

3A. The ionic radii refer to the most common oxidation states 3+ (except for Eu and Yb where it is 2+).

The radii change by a small amount from one element to the next, except of course for  $\text{Eu}^{\text{II}}$  and  $\text{Yb}^{\text{II}}$ . The radii contractions are only approximately linear; they are a little larger for the light than for the heavy elements; see also Figure 2.

**4.2. Molecular Bond Lengths.** The bond lengths of  $\text{LnH}$ ,  $\text{LnF}$ , and  $\text{LnO}$  are displayed in Figure 3, B, C, and D. The available experimental bond distances of the free molecules are taken over from refs 40, 52, and 57, and from the experimental papers of refs 28–32. In some cases it is not quite clear whether the experimental value refers to the same configuration and state of the different  $\text{LnX}$  molecules. This holds especially for  $\text{LaH}$  ( $f^0 s^2 \sigma^2$ )<sup>1</sup> $\Sigma^+$ , where we have chosen a value of  $R = 2.10$  Å.<sup>29,53</sup> In addition to our density functional results we also present the pseudopotential-CISD results<sup>39,52,54</sup> by Dolg et al. using a frozen or unfrozen 4f shell. The approximate lanthanide contractions from La to Lu are summarized in Table 5.

The density functional approach reproduces the measured trends quite well. Also the Yb irregularity is recovered. The

TABLE 5: Lanthanide Contractions from La to Lu

	$\Delta R_e^{\text{La-Lu}} (\text{\AA})$		
	expt <sup>29,53</sup>	DF(F)	PP(CISD) <sup>39-41,52,54</sup>
LnH	0.19(?)	0.19	0.07 (0.12 – 0.15) <sup>a</sup>
LnF	0.11	0.10	0.09 (0.15 – 0.18) <sup>a</sup>
LnO	0.04	0.05 (0.20) <sup>a</sup>	0.02 (0.11 – 0.16) <sup>a</sup>

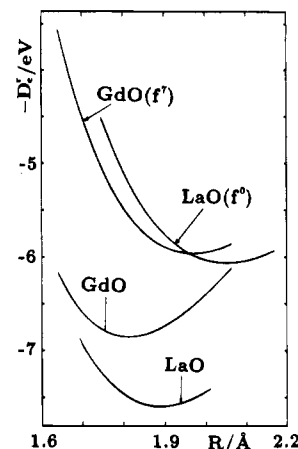
<sup>a</sup> Obtained with frozen 4f-shell.TABLE 6: DF(F) Results of LaO and GdO, Either with Optimized 4f and Outer Valence Shells or with 4f<sup>N</sup> Treated as a Frozen Core Shell and without Mixing 4f Basis Functions into the Outer-Valence Shell<sup>a</sup>

4f shell	LaO		GdO	
	optim	frozen	optim	frozen
$R_e^r$	1.89	2.05	1.82	1.97
$R_e^{\text{nr}}$	1.89	2.05	1.86	1.97
$D_e^r$	7.60	6.06	6.68	5.96
$D_e^{\text{nr}}$	8.82	6.61	9.60	6.61
$\omega_e^r$	761	642	810	698
$\omega_e^{\text{nr}}$	699	645	684	702
Mulliken Populations				
Ln				
4f	0.36	0.00	7.76	7.00
5d	1.12	1.31	0.76	1.33
6s	0.82	0.85	0.86	0.85
6p	0.16	0.11	0.05	0.12
O				
2s	1.93	1.98	1.97	1.95
2p	4.59	4.73	4.58	4.72
3d	0.02	0.02	0.02	0.01
$Q_{\text{Ln}}$	0.54	0.73	0.57	0.68
$-\mu$	3.73	4.51	2.90	4.50

<sup>a</sup> Bond distances  $R_e$  (in  $\text{\AA}$ ), dissociation energies  $D_e$  (in eV), and vibrational frequencies  $\omega_e$  (in  $\text{cm}^{-1}$ ), Mulliken populations, atomic gross charges  $Q$ , and dipole moments  $\mu$  (in D).

pseudopotential CISD bond lengths differ in two respects: (a) If the 4f populations are fixed to the integer values of the free atoms, the significant variation of the magnitude of the lanthanide contractions of LnH (large), LnF (medium), and LnO (small) is not recovered and the Yb irregularity is less developed; (b) if the 4f population is optimized, the lanthanide contractions become rather small. There is now no discrepancy concerning the lanthanide contractions of LnF (about 0.1  $\text{\AA}$ ) and LnO (very small).

**4.3. Variable 4f Population.** In Table 6 and Figure 4 we compare our DF(F) results of LaO and GdO with results where the atomic 4f-shell is treated as a frozen core shell in the molecules and where no unoccupied 4f functions are allowed to mix with the outer valence shell. The outer-valence configuration is  $1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4$ . The  $1\sigma$ -MO is of O 2s lone pair type, and the  $3\sigma$ -MO is weakly antibonding with dominant Ln 6s character.  $2\sigma$  and  $1\pi$  are O 2p-type MOs responsible for ionic and covalent bonding to the lanthanide atom. Because of Pauli repulsion (overlap) between the occupied O 2p<sub>z</sub> and the Ln 5sp-core, the  $1\pi$  is more bonding than the  $2\sigma$ . Upon relaxing the occupied 4f shell and allowing unoccupied 4f functions to mix into the outer-valence shell, 0.1–0.2 electrons are transferred from O 2p to Ln 4f. Furthermore, the admixture of Ln 5d to several MOs is significantly reduced in favor of Ln 4f admixture. This electronic rearrangement is driven by a

Figure 4. Potential curves of LaO and GdO with optimized 4f valence shell and with 4f<sup>N</sup> treated as a frozen core shell (LaO 4f<sup>0</sup> and GdO 4f<sup>7</sup>).

significant energy stabilization at short internuclear separations, resulting in 0.15  $\text{\AA}$  bond contraction. As Field<sup>59</sup> formulated, the essentially O<sup>2-</sup>-based valence orbital shapes itself by mixing in Ln AOs to get as close as possible to the Ln<sup>n+</sup> core without suffering overlap repulsion. The transfer of electronic charge to the 4f shell of the positive Ln reduces the bond polarity. We also note the pronounced increase of relativistic effects.

If two similar physical systems in their optimized ground states are compared, the following two rules hold: a polar covalence is more stable than the nonpolar counterpart (Pauling's electronegativity rule<sup>55</sup>); and the effective radius of Ln in the formal f<sup>N+1</sup> state is about 0.1  $\text{\AA}$  larger than that of Ln in the formal f<sup>N</sup> state. Above, however, we have compared the physical ground state of LnO (the Ln in its formal f<sup>N</sup> state with optimized 4f shell) with an *unphysical* state of LnO with frozen 4f<sup>N</sup> valence shell. Now the less polar, i.e., optimized, covalence is more stable, and the effective radius of Ln is decreased for increased 4f population.

**4.4. Bond Rigidity.** In principle, the total energy  $E$ , and its derivative  $E'$  and  $E''$  with respect to the internuclear distance, are independent of each other. In the case of similar bonds, however, the independent differences  $\Delta D_e$ ,  $\Delta D'_e \sim \Delta R_e$ , and  $\Delta D''_e \sim \Delta \omega_e$ , are sometimes found to be proportional or linear dependent, as stated by Badger's<sup>45</sup> ( $\Delta R \sim -\Delta \omega$ ) and Gordy's rules<sup>44</sup> ( $\Delta R \sim -\Delta D_e$ ). Here we have found that these latter rules do *not* hold for the relativistic/nonrelativistic differences of bonds. On the other hand, there exist relations between  $\Delta R^{\text{La-Lu}}$  and the force constant of the bonds  $k = E''$ , or the bond energies  $D_e$  (see Table 7), that is, something which may be called the "bond rigidity".

The interaction between atoms results in attractive and repulsive forces which are equal at the equilibrium bond length  $R_e$ . Attractive ones are the electrostatic (so-called quasiclassical) forces between two spherical neutral overlapping atoms, the orbital relaxation and orbital interactions upon bond formation, and the relativistic mass-velocity correction. The repulsive forces are due to the Pauli exclusion of occupied orbitals, and due to relativistic nuclear shielding, quenching of spin-orbit coupling, and the Darwin correction.<sup>47</sup> If one models the

TABLE 7: Lanthanide Molecules with Soft and Rigid Bonds

bond rigidity	molecules	$k(\text{N/cm})$	$D_e/\text{eV}$	$F(\text{eV}/\text{\AA})$	$\xi = (kD_e)^{1/2}$	$\Delta R^{\text{La-Lu}}(\text{\AA})$
soft bonds	Ln-H	$\sim 1$	$\sim 3$	$\sim 12$	$\sim 1.75$	0.19
medium bonds	Ln-F	$\sim 3$	$\sim 6$	$\sim 30$	$\sim 4$	0.11
rigid bonds	Ln=O	$\sim 5$	$\sim 7^{1/2}$	$\sim 54$	$\sim 6$	0.04



molecular energy curves by Lennard-Jones type potentials

$$V_{LJ} = A_{LJ}/R^m - B_{LJ}/R^n$$

the corresponding attractive and repulsive forces at  $R_e$  are

$$F_{att} = F_{rep} = (mn)^{1/2}/(m-n)(kD_e)^{1/2}$$

For a Morse potential

$$V_M = A_M \exp(-(k/D_e)^{1/2}R_e) - B_M \exp(-(k/D_e)^{1/2}R/2)$$

with  $A_M = D_e \exp((k/D_e)^{1/2}R_e)$ , and  $B_M = (4D_e A_M)^{1/2}$ , the forces at  $R_e$  are

$$F_{att} = F_{rep} = (kD_e)^{1/2}$$

The calculated forces at equilibrium internuclear distance<sup>47</sup> (see Table 7) also correlate linearly with  $(kD_e)^{1/2}$ . Therefore, we define the bond rigidity as  $\zeta = (kD_e)^{1/2}$ .

Obviously the bond lengths of the lanthanide molecules cannot be represented as a simple sum of constant atomic radii. In addition to the dependence of the lanthanide radii on the formal valence or formal  $f$  occupation and on the coordination number, the radii also depend on the deviation  $\Delta n_f$  of the  $f$  population from its formal, integer value, and on the rigidity  $\zeta$  of the bond. For the diatomics under investigation we write accordingly

$$R_{Ln-X} = R_X^0 + R_{Ln} \quad (2)$$

Here  $R_X^0$  and  $R_{Ln}$  are the covalent radii of  $X$  and  $Ln$ , the latter for  $4f^N$ -core (and coordination number 1 in the underlying case). As the reference value, we choose  $R^0(F) = 0.61 \text{ \AA}$  (this is the covalent radius of  $F$  in organic compounds  $R-F$ ). The lanthanide radius varies from  $La$  to  $Lu$ , to first order linearly  $\sim -\Delta R N/14$ ,  $N = 0-14$ . The lanthanide contraction  $\Delta R$  is large for soft bonds and smaller for rigid bonds. So we write  $\Delta R = a - b\zeta$ , i.e.

$$R_{Ln} = R_{La}^0 - (a - b\zeta_{LnX})N/14 \quad (3)$$

The parameters which reproduce the experimental bond lengths nearly exactly are presented in the first line of Table 8. Alternatively to  $\zeta$ , we could also have used the bond energy  $D_e$  or the force constant  $k$  with similar success; for instance

$$R_{Ln}/(\text{pm}) = 142 - (23 - 3.4k(\text{cm/N}))N/14 \quad (4)$$

The effective radius of  $O$  is smaller than the one of  $F$  by approximately the same amount as  $H_2C=O$  is shorter than  $H_3C-F$  ( $138 - 121 = 17 \text{ pm}$ ). The effective radius of hydrogen is comparatively large, indicating its weak bonding to  $Ln$ . As is to be expected, the present lanthanide radii for coordination number 1 are smaller than the ones given in the literature for  $CN = 3$  (e.g.,  $R_{La} = 169 \text{ pm}$ <sup>50</sup>) by the typical amount of  $1/4 \text{ \AA}$ .

In the case of the calculated bond lengths, the linear regression (eqs 2 and 3) can still be improved somewhat by taking also the  $4f$  Mulliken population as a parameter to determine the effective radius of  $Ln$ . This yields  $8 \text{ pm}$  bond contraction (see Table 8), if the outer-valence shell is stabilized by admixture of  $4f$  basis functions corresponding to 1 additional unit  $\Delta n$  of  $4f$  Mulliken population.

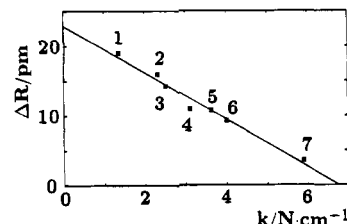
## 5. Summary and Conclusions

Density functional calculations including correlation ( $C$ ) and in addition also nonlocal exchange corrections ( $F$ ) have been

**TABLE 8: Effective Atomic Radii and Lanthanide Contraction (in pm) for  $LnX$  Molecules (See Eqs 2 and 3)**

source	$R_F^0$	$R_H^0$	$R_O^0$	$R_{La}^0$	$\Delta R = a - b\zeta$
exp $R_e$	61	69	42.5	141	$27 - 3.5\zeta(\text{cm/N eV})^{1/2}$
calcd $R_e$	61	65	44.5	144	$27 - 3.2\zeta(\text{cm/N eV})^{1/2}$
	61	61.5	45.5	147	or $25 - 2.4\zeta(\text{cm/N eV})^{1/2} - 8\Delta n_f$

<sup>a</sup> Reference value. <sup>b</sup> For inactive  $4f$  shell ( $\Delta n_f = 0$ ), soft bond ( $\zeta = 0$ ) and coordination number 1.



**Figure 5.** Lanthanide contraction  $\Delta R$  ( $\Delta R = R_{LaX} - R_{LuX}$  or  $\Delta R = R_{BaX} - R_{YbX}$ , in pm) of seven lanthanide diatomic series, versus average force constant  $k$  (in  $N/cm$ ). Data from ref 57. (1)  $Ln^+(f^{N+1}\sigma_{6s}^1) H^-$  ground states; (2)  $Ln^+(f^{N+1}\sigma_{6s}^1) O^-(2p^{-1})$  excited states; (3)  $Ln^+(f^{N+1}\sigma_{6s}^1) F^-$  excited states; (4)  $Ln^+(f^{N+1}\sigma_{6s}^1) F^-$  excited states; (5)  $Ln^+(f^N\sigma_{6s}^2) F^-$  ground states; (6)  $Ln^{2+}(f^{N+1}) O^{2-}$  excited states; (7)  $Ln^{2+}(f^N\sigma_{6s}^2) O^{2-}$  ground states.

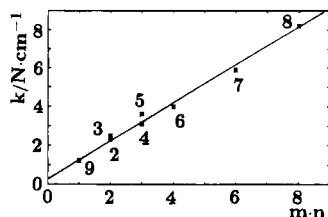
carried out on lanthanide compounds  $LnH$ ,  $LnF$ , and  $LnO$  ( $Ln = La, Gd, Yb, Lu$ ). Compared to other methods (semiempirical or pseudopotential), density functional calculations are not worse or even better concerning bond lengths, bond energies, and vibrational frequencies. For bond lengths, DF(F) gives values up to a few picometers too large, comparable to the typical errors in light atomic systems. For bond energies and frequencies, DF(F) gives astonishingly good results. Relativistic bond length corrections are negative but not significant. Relativistic corrections to vibrational frequencies and especially to bond energies are important.

The different experimental lanthanide contractions for different kinds of lanthanide compounds are reproduced by the present calculations. They are  $0.19 \text{ \AA}$  for  $LnH$ ,  $0.10 \text{ \AA}$  for  $LnF$ , and  $0.05 \text{ \AA}$  for  $LnO$ . Standard bond length rules are unsatisfactory in explaining this. We have found two factors, with the help of which we can rationalize this finding.

First, it is a quite common rule that the stronger a bond (large  $k$  and  $D$ ) the shorter it is. The effective radii of strongly bonding ligands are small (compare  $R(O)$  with  $R(H)$ ). A large bond force does not tolerate much bond expansion when going from  $Lu$  to  $La$ . For bonds with  $k > 7 \text{ N cm}^{-1}$ ,  $D > 9 \text{ eV}$ , and  $\zeta > 8$  the lanthanide contraction should nearly vanish. Extrapolating to vanishing bond strength, we obtain a lanthanide contraction of about  $25 \text{ pm}$ . This is larger than the contraction of the outer core  $5p$  and smaller than of the outer-valence  $6s$  AOs of the free lanthanide atoms. The dependence of the lanthanide contraction on the bond rigidity does not only hold for the molecular ground states but also for excited states with modified bond strengths, as demonstrated in Figure 5.

A similar behavior as for the bond lengths is observed also for the vibrational frequencies. The latter increase smoothly in the case of  $MX$  molecules<sup>28</sup> when varying the metal  $M$  along the series  $Cs, Ba, (La/Lu), Hf, Ta, W$ . However,  $LaX$  and  $LuX$  do not have the same  $\omega$  but there is a step of  $13.6\%$  ( $187 \text{ cm}^{-1}$ ) for the weakly bound hydrides,  $7.4\%$  ( $42 \text{ cm}^{-1}$ ) for the fluorides, and only  $3.6\%$  ( $29 \text{ cm}^{-1}$ ) for the strongly bound oxides.

Second, the  $4f$  shell may participate in bonding. Within the superconfiguration model, the  $4f$ -shell orbitals are equally occupied by, say,  $N$  electrons. We have allowed the occupied  $4f$  orbitals to relax according to the electron distribution in the outer-valence shell. More important, however, is the admixture



**Figure 6.** Average force constants  $k$  versus the products of formal charges  $mn$ , of seven lanthanide diatomic molecular series  $\text{Ln}^{m+}(\text{ov})^{m-n}\text{X}^{n-}$  (see legend of Figure 5) and of the (8)  $\text{Hf}^{2+}(\text{f}^4\sigma^2)\text{O}^{2-}$  ground state, and (9) the  $\text{Cs}^+(\text{f}^0\sigma^0)\text{F}^-$  ground state.  $m+$  is the formal charge of the lanthanide core;  $(m-n)$  is the number of electrons in the outer valence shell (ov).

of unoccupied 4f orbitals into the outer-valence shell, as indicated by the Mulliken populations. Going from Lu to La, i.e., to lower nuclear charges, the Ln–X bonding becomes weaker in general. There is a counteracting trend, however, in the case of strongly binding ligands at short distance, like O: unoccupied 4f orbitals of the lighter lanthanides can participate in and strengthen the bonding (compare also Gotkis<sup>56</sup>). This effect is already quite pronounced in GdO and even larger in LaO.

Finally, we corroborate Dolg's<sup>40</sup> finding that most lanthanide diatomics also show significant 5d participation in bonding. This does not mean that 5d<sup>1</sup> atomic configurations need be used in simple models such as ligand field theory. However, 5d admixture to the outer-valence shell MOs is important, for instance, to obtain a reliable charge distribution and dipole moment (compare section 4.5 of ref 12 and ref 59).

We also note that formal charges such as in  $\text{Ln}^+\text{H}^-$ ,  $\text{Ln}^+\text{F}^-$ , and  $\text{Ln}^{2+}\text{O}^{2-}$  do not correspond to the real charge distribution (or to the dipole moments<sup>12</sup>). Nevertheless they form the basis of very useful models. Field et al.,<sup>53,57–59</sup> for instance, modeled and predicted the relative energies, electronic symmetries, configurational characters, bond lengths, and vibrational frequencies of ground and excited states (up to 3 eV) of LnX molecules quite successfully. As an example, we present in Figure 6 the astonishingly good correlation between the force constants<sup>57</sup> of  $\text{Ln}^{m+}(\text{ov})^{m-n}\text{X}^{n-}$  and the products of integer charges  $mn$ , where  $m$  is the formal charge of the core of the lanthanide atom and  $m-n$  is the number of outer-valence electrons (ov). (The LnH series does not fit into the correlation of oxides and fluorides and is omitted in Figure 6. Field<sup>57</sup> has pointed out that in the case of diffuse valence electron clouds and steep repulsion between closed core shells (which do not exist for H), the force constant should be proportional to the product of the formal charges of the atomic core ions.)

In this context we mention another paradox, concerning strongly polar compounds: the potential curves of alkali halide molecules are very well modeled by Rittner's point charge approach,<sup>60</sup> and the lattice energies of crystalline salts can accurately be determined with the help of Madelung energies. According to Seiler and Dunitz,<sup>61</sup> the fact that it is easier to calculate many properties with point charges than with charge distributions makes ionic point charge models very convenient, but it does not necessarily make them more correct (see also ref 62).

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