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Pseudopotential study of lanthanum and lutetium dimers

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Abstract. Relativistic energy-consistent small-core lanthanide pseudopotentials of the Stuttgart–Bonn variety and extended valence basis sets have been used for the investigation of the dimers La_2 and Lu_2. It was found that the ground states for La_2 and Lu_2 are most likely $^1\sum_g{}^+$ ($\sigma_g{}^2\pi_u{}^4$) and $^3\sum_g{}^-$ ($4f^{14}4f^{14}\sigma_g{}^2\sigma_u{}^2\pi_u{}^2$), respectively. The molecular constants including error bars were derived from multireference configuration interaction as well as coupled-cluster calculations, taking into account corrections for atomic spin–orbit splitting as well as possible basis set superposition errors. The theoretical values for La_2 ($R_e = 2.70 \pm 0.03$ Å, $D_e = 2.31 \pm 0.13$ eV, $\omega_e = 186 \pm 13$ cm^{-1}) show good agreement with the experimental binding energy ($D_e = 2.52 \pm 0.22$ eV), but the experimental vibrational constant in an Ar matrix ($\omega_e = 236 \pm 0.8$ cm^{-1}) is significantly higher. For Lu_2 the theoretical values ($R_e = 3.07 \pm 0.03$ Å, $D_e = 1.40 \pm 0.12$ eV, $\omega_e = 123 \pm 1$ cm^{-1}) are in overall excellent agreement with experimental data ($D_e = 1.43 \pm 0.34$ eV, $\omega_e = 122 \pm 1$ cm^{-1}). The electronic structures of La_2 and Lu_2 are compared to those other lanthanide dimers and trends in the series are discussed.

Key words: Lanthanum dimer – Lutetium dimer – Pseudopotentials – Spectroscopic constants

1 Introduction

Lanthanum and lutetium stand at the beginning and the end of the lanthanide series, respectively. Their atomic ground-state configurations (La $5d6s^2$, Lu $4f^{14}5d6s^2$) involve a filled 6*s* shell along with an unpaired 5*d* electron. Besides these genuine valence shells, the low-lying 6*p* virtual orbitals may also participate in chemical bonding. The availability of valence orbitals with various main and angular quantum numbers allows complex bonding situations. This has already been encountered for the light homonuclear rare-earth dimers Sc_2 [1] and Y_2 [2] and is especially true for the dimers La_2 and Lu_2 owing to larger relativistic effects. It is interesting to study these two dimers not only because they have seldom been theoretically investigated before [3, 4, 5], but also since they are probably among the simplest representatives of the homonuclear lanthanide dimers. For almost all other members of the series the effect of the partially occupied 4*f* shell has also to be taken into account, including the possible participation in chemical bonding. At the same time La_2 and Lu_2 allow the study of the change in bonding owing to the lanthanide contraction, which is known to be mainly a shell-structure effect due to the incomplete shielding of the valence electrons from the increasing nuclear charge by the 4*f* shell and is enhanced further by the increase in the relativistic effects along the series.

Very few experimental results are available for La_2 and Lu_2. The most recent experimental data on La_2 and Lu_2 were obtained in 2000 by Liu et al. [6] and Fang et al. [7], using Raman and absorption spectroscopy in Ar matrices. The measured ground-state vibrational constants, ω_e, are 236.0 ± 0.8 cm^{-1} for La_2 and 121.6 ± 0.8 cm^{-1} for Lu_2. From these data and the anhamonicities, $\chi_e\omega_e$, the spectroscopic dissociation energies of 1.8 ± 0.3 and 2.9 ± 1.8 eV for La_2 and Lu_2, respectively, have been estimated. These values differ substantially from the thermochemically determined dissociation energies of 2.52 ± 0.22 eV for La_2 [8] and 1.43 ± 0.34 eV for Lu_2 [8]. The bond length for La_2 was estimated to be 2.80 Å by Verhaegen et al. [9]. To our knowledge the bond length has not been determined for Lu_2. Another piece of information available about La_2 is the failure of Knight et al. [10] to observe an electron spin resonance spectrum attributable to La_2; therefore a possible $^1\sum_g^+$ ground state was suggested.

One of the present authors did quantum chemical configuration interaction (CI) and correlation energy density functional calculations on several lanthanide dimers by using scalar-relativistic-energy-adjusted ab

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initio pseudopotentials modeling lanthanide elements with fixed integral 4*f* occupation numbers [4]. The spectroscopic constants of the proposed ground states, i.e., La_2 $\sigma_g{}^2\sigma_u{}^1\sigma_g{}^1\pi_u{}^2$ $^5\sum_u^-$ ($R_e = 3.25$ Å, $\omega_e = 130$ cm^{-1}, $D_e = 1.17$ eV) and Lu_2 $\sigma_g{}^2\sigma_u{}^2\sigma_g{}^2$ $^1\sum_g^+$ ($R_e = 3.79$ Å, $\omega_e = 74$ cm^{-1}, $D_e = 0.55$ eV), are in disagreement with the current set of experimental values. The most recent theoretical results for Lu_2 were obtained by Baştuğ et al. [5] in 1999, with relativistic gradient-corrected density functional theory (DFT). The constants $R_e = 2.51$ Å, $\omega_e = 174$ cm^{-1} and $D_e = 2.39$ eV were published, but a corresponding ground-state assignment has not been made. In view of the substantial differences between the theoretical results and the experimental data we felt that a reinvestigation of the dimers La_2 and Lu_2 at the ab initio level is timely.

Recently we have developed new valence basis sets (14s13p10d8f6g)/[6s6p5d4f3g] for relativistic energy-consistent small-core (28 core electrons) lanthanide pseudopotentials [11], which include the 4*f* shell explicitly in the valence. A generalized contraction scheme based on atomic natural orbital coefficients was adapted and several g functions are included to polarize and correlate the 4*f* shell. Test calculations using the new basis sets gave very good agreement with experimental results for numerous diatomic lanthanide compounds (Ln*X*, Ln = La, Lu, Gd, Yb, Eu, *X* = H, O, F, S) [11, 12]. Here, we report the calculated spectroscopic constants of La_2 and Lu_2 using the new basis sets in connection with large-scale correlation treatments. On the basis of our calculations we assign a singlet ground state ($^1\sum_g{}^+$) for La_2 and a triplet ground state ($^3\sum_g{}^-$) for Lu_2. A comparison with the homonuclear dimers of other trivalent (Ce_2, Gd_2) and divalent (Eu_2, Yb_2) lanthanides is also made.

2 Method

The relativistic energy-consistent small-core pseudopotentials used in this work for La, Ce, Eu, Yb and Lu have been published elsewhere [11, 13]. The 1*s*–3*d* shells were included in the pseudopotential core, while all shells with a main quantum number larger than 3 were treated explicitly. Recently developed Gaussian (14s13p10d8f6g)/[6s6p5d4f3g] atomic natural orbital valence basis sets were applied [11]. In case of the ground states, the standard basis sets (14s13p10d8f6g)/[6s6p5d4f3g] were augmented by a diffuse (3s3p3d3f3g) set.

The complete-active-space self-consistent-field (CASSCF) method was used to generate the orbitals for the subsequent multireference CI (MRCI) calculations. In the CASSCF calculations the 4*s*, 4*p*, 4*d*, 5*s*, 5*p* and for Lu in addition the 4*f* orbitals were kept doubly occupied. Firstly, the lowest σ, π and δ valence orbitals of gerade and ungerade parity, arising mainly from the 5*d*, 6*s* and 6*p* atomic orbitals, were chosen as the active space for the valence electrons (six electrons in ten orbitals). However, the MRCI expansions based on these active spaces were too large to handle with our current computer facilities. Therefore, we selected all natural orbitals with significant occupations (greater than 0.01 for La_2, greater than 0.03 for Lu_2) as a new reduced active space and to generate the corresponding initial molecular orbitals for the subsequent internally contracted MRCI calculations. For the molecular ground states $2\sigma_g$, $1\sigma_u$, $2\pi_g$, $2\pi_u$, $1\delta_g$ (La_2, eight orbitals) and $2\sigma_g$, $1\sigma_u$, $2\pi_g$, $2\pi_u$ (Lu_2, seven orbitals) valence orbitals defined the new active spaces. Clearly this active space is not what one would choose on the basis of physical arguments such as a proper dissociation into two neutral atoms (e.g., six electrons in 12 orbitals, i.e., 5*d* and 6*s* on each atom), but at least near the equilibrium distance it is a fairly good approximation. The MRCI configuration space was obtained by single and double excitations with respect to the CASSCF reference wavefunction. The 4*s*, 4*p* and 4*s*, 4*p*, 4*d* orbitals were frozen in the MRCI calculations using the standard basis sets for La_2 and Lu_2 respectively. Whereas in the MRCI calculations using the extended basis sets 4*s*, 4*p*, 4*d* orbitals were frozen for both La_2 and Lu_2. The number of reference configuration state functions the size of the MRCI matrix after (before) contraction for the ground states in D_{2h} symmetry were 174/1.6×10^7 (3.7×10^8) for La_2 and 74/1.2×10^7(3.3×10^8) for Lu_2 using the standard basis sets. Since even larger configuration expansions arise for excited states, we did not allow for excitations from the 5*s* and 5*p* orbitals in their investigations. Still the size of the calculations, for example, 174/9.0×10^6 (2.0×10^8) for Lu_2 $^1\sum_g{}^+$ or 144/8.9×10^6 (2.0×10^8) for Lu_2 $^1\sum_g{}^-$, is at the limit of our current hardware capabilities. In order to take into account the effects of 5*s* and 5p correlation at least in an approximate manner, we extracted only the excitation energies from these calculations and added them to the ground-state potential curve obtained with the larger active orbital space.

Many of the low-lying electronic states of La_2 and Lu_2 have a significant multireference character. In a few cases however, for example, for the ground states of both dimers, high-level single-reference treatments appear reasonable. We therefore performed additional coupled-cluster singles and doubles calculations with a perturbative treatment of triples [CCSD(T)] as an alternative to the CASSCF/MRCI approach. Excitations were allowed from the $\sigma_g{}^2\pi_u{}^4$ valence orbitals and the 4*d*, 5*s* and 5*p* inner shells for La_2 $^1\sum_g{}^+$, whereas they were allowed from the $\sigma_g{}^2\sigma_u{}^2\pi_u{}^2$ valence orbitals and the 4*d*, 4*f*, 5*s* and 5*p* inner shells for Lu_2 $^3\sum_g{}^-$. A similar active orbital space was chosen for the study of selected excited states.

The program system MOLPRO [14] was used to perform the calculations. The spectroscopic constants were derived by fitting a fifth-degree polynomial in the interatomic distance, *R*, times a factor $1/R$ for six points on the potential curve near the equilibrium distance. A spacing of 0.1 au between the points was used. Tests with different fitting functions, including least-squares fits, indicate that the accuracy of the molecular constants derived is better than 0.001 Å for bond lengths, 0.001 eV for binding energies and 1 cm^{-1} for vibrational frequencies. The binding energies were calculated with respect to the separated atoms in the ground state at a distance of 50 au, in order to correct the size-inconsistency of the CI calculations.

3 Results and discussion

La and Lu both have a $5d^1 6s^2$ ^{2}D ground state. Both elements also have a low-lying $5d^2 6s^1$ ^{4}F excited state, which is much more favorable for bonding. However, the experimental ^{2}D–^{4}F promotion energy for La (0.33 eV) is much lower than that of Lu (2.34 eV) [15]; therefore, La_2 is expected to exhibit stronger bonding than Lu_2 [6]. Moreover, although La and Lu have the same ground state and low-lying excited state, a different electronic structure may be expected for La_2 and Lu_2, mainly owing to relativistic effects. These lead to a contraction and stabilization of the 6*s* shell and an expansion and destabilization of the 5*d* shell. From a comparison of nonrelativistic Hartree–Fock with scalar-relativistic Wood–Boring all-electron values [16], one finds the relativistic $<r>$-expectation values for 6*s* of La, Ce, Gd and Lu to be 0.21, 0.22, 0.28 and 0.36 au shorter and for 5*d* to be 0.13, 0.13, 0.16 and 0.25 au longer than the nonrelativistic results (Table 1). The increasing impact of relativistic effects along the lanthanide series is obvious. For the valence orbital energies even a

Table 1. $<r>$-expectation values and negative orbital energies, $-\varepsilon$ (au), for the 5*d* and 6*s* valence orbitals of La, Ce, Gd and Lu ($n = 0, 1, 7, 14$) in their $4f^n5d^16s^2$ ground-state configurations from nonrelativistic (Hartree–Fock, *HF*) and scalar-relativistic (Wood–Boring, *WB*) all-electron calculations. Experimental promotion energies (*PE*) from Ref. [15] of the excited $4f^n5d^26s^1$ state with respect to the $4f^n5d^16s^2$ ground state. The PE of the excited $4f^{14}6s^26p^1$ state is given in *parentheses*

Metal	$<r>_d$ (au)		$<r>_s$ (au)		$-\varepsilon_d$ (au)		$-\varepsilon_s$ (au)		PE (eV) Experiment
	HF	WB	HF	WB	HF	WB	HF	WB	
La	2.758	2.890	4.931	4.722	0.269	0.236	0.170	0.180	0.33
Ce	2.714	2.843	4.869	4.648	0.270	0.236	0.173	0.183	0.29
Gd	2.552	2.708	4.554	4.276	0.265	0.223	0.185	0.200	0.79
Lu	2.485	2.738	4.259	3.903	0.243	0.188	0.199	0.222	2.34(0.72)

reversal of the ordering of the 5*d* and 6*s* orbital is observed, i.e. $\varepsilon_{6s} > \varepsilon_{5d}$ for La and $\varepsilon_{6s} < \varepsilon_{5d}$ for Lu (table 1). This explains the higher $5d^16s^2\ ^2D \rightarrow 5d^26s^1\ ^4F$ promotion energy of Lu (2.34 eV) compared to La (0.33 eV). The consequences for the electronic ground-state configurations of the dimers is discussed later. For Lu, the 6*p* orbital is also expected to contribute significantly to chemical bonding, since the promotion energy from the ground-state $4f^{14}5d^16s^2\ ^2D$ to $4f^{14}6s^26p^1\ ^2P$ is 0.72 eV, which is 1.62 eV lower than the promotion energy to $4f^{14}5d^26s^1\ ^4F$.

Many low-lying states for La_2 and Lu_2 were calculated in the present study and the results for some of them are listed in Tables 2 and 3, respectively. A singlet ground state $^1\sum_g{}^+$ ($\sigma_g{}^2\pi_u{}^4$) and a triplet ground state $^3\sum_g{}^-$ ($4f^{14}4f^{14}\sigma_g{}^2\sigma_u^2\pi_u^2$) were obtained for La_2 and Lu_2, respectively. The calculated spectroscopic constants of Lu_2 obtained at the MRCI level with the cluster correction of Siegbahn (MRCI + Q) ($R_e = 3.072$ Å, $\omega_e = 124$ cm^{-1}, $D_e = 1.73$ eV) and at the CCSD(T) level ($R_e = 3.058$ Å, $\omega_e = 122$ cm^{-1}, $D_e = 1.67$ eV) are in excellent agreement with available experimental results ($\omega_e = 121.6 \pm 0.8$ cm^{-1} [7], $D_e = 1.43 \pm 0.34$ eV [8]). The large basis set (standard basis set augmented by a diffuse set) gives only small corrections with respect to the standard basis set at the MRCI + Q/CCSD(T) level for the bond length (0.032/0.053 Å shorter) and the vibrational frequencies (1/4 cm^{-1} higher). However, the binding energies are 0.44/0.53 eV larger than the ones obtained with the standard basis set. For the ground state, the CCSD(T) results are very similar to the CCSD results. The differences for the bond length, the binding energy and the vibrational frequency are at most 0.009 Å, 0.20 eV and 3 cm^{-1}, respectively. In case of the excited states, the CCSD(T) values differ noticeably from the CCSD results, i.e., the differences for the bond lengths, the binding energies and the vibrational frequencies are at most 0.03 Å, 0.47 eV and 13 cm^{-1}, respectively.

Table 2. Bond lengths, R_e, vibrational constants, ω_e, and binding energies, D_e, for selected states of La_2. Small-core pseudopotentials (*SPP*) (28 core electrons); large-core pseudopotentials (*LPP*) (46 core electrons for La, 60 core electrons for Lu); counterpoise correction of the basis set superposition error (*CPC*); core-polarization potential (*CPP*); multireference configuration interaction (*MRCI*) with the cluster correction of Siegbahn (*MRCI + Q*); density functional theory calculations with gradient-corrected exchange according to Becke [17] and correlation according to Perdew [18] (*BP*)

State[a]	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	Pseudopotentials	Method
a $^3\Delta_g$	2.635/2.659	0.81/1.26	245/228	SPP	CCSD/CCSD(T)[c]
b $^3\sum_g{}^-$	2.896/2.936	0.88/1.39	159/143	SPP	CCSD/CCSD(T)[c]
c $^3\sum_g{}^+$	2.691/2.718	0.93/1.41	240/225	SPP	CCSD/CCSD(T)[c]
d $^5\sum_u{}^-$	3.078/3.108	1.34/1.62	111/111	SPP	CCSD/CCSD(T)[c]
e $^3\Pi_u$	2.756/2.780	1.56/2.01	195/183	SPP	CCSD/CCSD(T)[c]
f $^1\sum_g{}^+$	2.649/2.666	1.88/2.32	225/217	SPP	CCSD/CCSD(T)[c]
	2.657/2.675	1.72/2.15	224/214	SPP	CPC, CCSD/CCSD(T)[c]
	2.655/2.671	2.12/2.59	211/198	SPP	CCSD/CCSD(T)[d]
	2.673/2.694	1.89/2.34	202/188	SPP	CPC, CCSD/CCSD(T)[d]
	2.640/2.655	2.12/2.53	218/206	LPP, CPP	CCSD/CCSD(T)[e]
	2.676/2.695	1.88/2.29	202/188	LPP, CPP	CPC, CCSD/CCSD(T)[e]
	2.727/2.695	2.25/2.42	194/200	SPP	MRCI/MRCI + Q[c]
	2.734/2.701	2.50/2.60	174/183	SPP	MRCI/MRCI + Q[d]
	2.710/2.677	2.52/2.62	181/191	LPP, CPP	MRCI/MRCI + Q[e]
	≈2.80 [19][b]	2.52 ± 0.22 [8]	236 ± 0.8 [6]		Experiment
	2.606	2.75	229	SPP	BP

[a] Leading (reference) configuration a, $\sigma_g^2\sigma_u^2\sigma_g^1\delta_g^1$; b, $\sigma_g^2\sigma_u^2\pi_u^2$; c, $\sigma_g^2\sigma_u^2\sigma_g^1\sigma_g^1$; d, $\sigma_g^2\sigma_u^1\sigma_g^1\pi_u^2$; e, $\sigma_g^2\sigma_u^2\sigma_g^1\pi_u^1$; f, $\sigma_g^2\pi_u^4$

[b] Estimated value

[c] Standard basis set (14*s*13*p*10*d*8*f*6*g*)/[6*s*6*p*5*d*4*f*3*g*]; 4*s*, 4*p* frozen in MRCI and CCSD(T)

[d] Standard basis set (14*s*13*p*10*d*8*f*6*g*)/[6*s*6*p*5*d*4*f*3*g*] augmented by a diffuse (3*s*3*p*3*d*3*f*3*g*) set, 4*s*, 4*p*, 4*d* frozen MRCI; 4*s*, 4*p* frozen in CCSD(T)

[e] Standard basis set (7*s*6*p*5*d*)/[5*s*4*p*3*d*] augmented by (2*s*2*p*2*d*5*f*3*g*)

Table 3. Bond lengths, vibrational constants and binding energies for selected states of Lu_2

State[a]	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	Pseudopotentials	Method
a $^{1}\sum_{g}{}^{+}$	2.499/2.525	−2.01/−1.54	186/173	SPP	CCSD/CCSD(T)[b]
	2.567/2.594	−1.35/−0.96	174/164	LPP, CPP	CCSD/CCSD(T)[d]
b $^{5}\sum_{u}{}^{-}$	2.807/2.801	−0.16/0.10	144/146	SPP	CCSD/CCSD(T)[b]
c $^{1}\sum_{g}{}^{-}$	3.197/3.163	0.75/0.71	107/108	SPP	MRCI/MRCI + Q[b]
c $^{1}\sum_{g}{}^{+}$	3.171/3.142	0.83/0.75	112/112	SPP	MRCI/MRCI + Q[b]
c $^{3}\sum_{g}{}^{-}$	3.061/3.064	1.15/1.33	124/121	SPP	CCSD/CCSD(T)[b]
	3.093/3.101	0.97/1.14	121/118	SPP	CPC, CCSD/CCSD(T)[b]
	3.043/3.034	1.62/1.82	124/124	SPP	CCSD/CCSD(T)[c]
	3.064/3.058	1.48/1.67	122/122	SPP	CPC, CCSD/CCSD(T)[c]
	3.076/3.079	1.59/1.73	121/120	LPP, CPP	CCSD/CCSD(T)[d]
	3.086/3.090	1.53/1.66	119/119	LPP, CPP	CPC, CCSD/CCSD(T)[d]
	3.094/3.083	1.79/1.78	121/121	LPP, CPP	MRCI/MRCI + Q[d]
	3.132/3.105	1.36/1.29	123/123	SPP	MRCI/MRCI + Q[b]
	3.108/3.072	1.78/1.73	121/124	SPP	MRCI/MRCI + Q[c]
		1.43 ± 0.34 [8]	121.6 ± 0.8 [7]		Experiment
	3.123	1.28	105	SPP	BP

[a] Leading (reference) configuration a: $4f^{14}4f^{14}\sigma_g^2\pi_u^4$; b: $4f^{14}4f^{14}\sigma_g^2\sigma_u^1\sigma_g^1\pi_u^2$; c: $4f^{14}4f^{14}\sigma_g^2\sigma_u^2\pi_u^2$

[b] Standard basis set (14*s*13*p*10*d*8*f*6*g*)/[6*s*6*p*5*d*4*f*3*g*], 4*s*, 4*p*, 4*d* frozen in MRCI; 4*s*, 4*p* frozen in CCSD(T)

[c] See footnote d to Table 2

[d] See footnote e to Table 2

The calculated binding energies for La_2 [MRCI + Q 2.60 eV, CCSD(T) 2.34 eV] bracket the experimental value ($D_e = 2.52 \pm 0.22$ eV [8]) and the bond lengths [MRCI + Q 2.701 Å, CCSD(T) 2.694 Å] are in reasonable agreement with the estimated experimental value (2.80 Å [9]). However, the vibrational frequencies [MRCI + Q 183 cm^{-1}, CCSD(T) 188 cm^{-1}] are significantly lower than the recent experimental result ($\omega_e = 236$ cm^{-1} [6]) obtained by Raman spectroscopy in an Ar matrix. The CCSD(T) values differ noticeably from the CCSD results for La_2, i.e., the bond lengths are 0.02–0.04 Å longer, the binding energies are 0.3–0.5 eV larger and the vibrational frequencies are 0–17 cm^{-1} lower. This emphasizes the greater importance of triple excitations for La_2 compared to Lu_2.

From our results calculated with the extended basis sets at the MRCI + Q and CCSD(T) level we obtain the following intermediate estimates and error bars of the molecular constants: La_2 $R_e = 2.686 \pm 0.015$ Å, $D_e = 2.595 \pm 0.005$ eV, $\omega_e = 190.5 \pm 7.5$ cm^{-1}; Lu_2 $R_e = 3.053 \pm 0.019$ Å, $D_e = 1.775 \pm 0.045$ eV, $\omega_e = 124 \pm 0$ cm^{-1}. It is not possible for us at present to estimate the magnitude of the counterpoise correction (CPC) at the MRCI + Q level, mainly owing to the necessary restrictions of the active space and the need to calculate D_e with respect to the separated atoms at large distances in order to roughly achieve size-extensivity. Therefore, the CPC was extracted at the CCSD(T) level and added to the estimates. It is known that the CPC tends to overestimate the basis set superposition error (BSSE). We therefore believe the true results to be bracketed by the estimates with and without CPC. The average of these values as well as the error bars derived from their maximum difference, i.e., also taking the difference between the MRCI + Q and CCSD(T) results into account, lead us to our final scalar-relativistic results for La_2 ($R_e = 2.70 \pm 0.03$ Å, $D_e = 2.47 \pm 0.13$ eV, $\omega_e = 186 \pm 13$ cm^{-1}) and Lu_2 ($R_e = 3.07 \pm 0.03$ Å, $D_e = 1.70 \pm 0.12$ eV, $\omega_e = 123 \pm 1$ cm^{-1}) in their ground states.

Spin–orbit effects cannot be neglected for atoms as heavy as La and Lu. From the experimental fine-structure splittings of the ^{2}D ground state [15] we estimate a maximum bond destabilization of 0.16 eV for La_2 and 0.30 eV for Lu_2. First-order spin–orbit effects vanish for the molecular ground states of $\sum$ symmetry and are neglected for simplicity, as are the small spin–orbit corrections for R_e and ω_e. The final theoretical binding energies are 2.31 ± 0.13 eV for La_2 and 1.40 ± 0.12 eV for Lu_2. With exception of ω_e for La_2 our theoretical values are in satisfactory agreement with available experimental data (Table 4). Since in our work we did not find a sufficiently low lying excited state (i.e., a possible candidate as a ground state) which has ω_e near the experimental value, we have on the basis of the present calculations no explanation for this disagreement. We note that our assignment of a $^{1}\sum_{g}{}^{+}$ ground state is in line with the failure to observe an electron spin resonance spectrum for La_2 [10].

DFT calculations using the gradient-corrected exchange according to Becke [17] and correlation according to Perdew [18] were also performed for the ground states of La_2 (Table 2) and Lu_2 (Table 3). The spectroscopic constants agree fairly well with the results from the correlated wavefunction-based ab initio methods, i.e., the differences for bond lengths, binding energies and vibrational frequencies are at most 0.09 Å, 0.5 eV and 46 cm^{-1}, respectively. Baştuğ et al. [5] calculated spectroscopic constants for Lu_2 ($R_e = 2.51$ Å, $\omega_e = 174$ cm^{-1}, $D_e = 2.39$ eV) using relativistic DFT at the all-electron level; however, the assumed ground-state configuration was not stated. The published bond length and vibrational frequency agree with the DFT results we obtained for the $^{1}\sum_{g}{}^{+}$ state ($\sigma_g{}^2\pi_u{}^4$, $R_e = 2.547$ Å, $\omega_e = 173$ cm^{-1}). However, whereas Baştuğ et al. find a strongly bound system with a binding energy almost 1 eV larger than the experimental value (1.43 ± 0.34 eV), we obtain no bonding at all for this state ($D_e = -1.23$ eV). At present we have no explanation for

Table 4. Bond lengths, vibrational constants and binding energies for selected lanthanide dimers. Averaged coupled-pair functional (*ACPF*)

Metal	State	R_e (Å)[a]	D_e (eV)[b]	ω_e (cm^{-1})[c]	Reference[e]
La	$\sigma_g{}^2\pi_u{}^4$, ${}^1\sum_g{}^+$	2.70 ± 0.03	2.31 ± 0.13	186 ± 13	This work
		≈2.80	2.52 ± 0.22	236 ± 0.8	Experiment
Ce	$4f^1(\varphi_u{}^1)4f^1(\varphi_g{}^1)\ \sigma_g{}^2\pi_u{}^4$, ${}^3\sum_u^+$	2.630	1.79	188	CCSD(T)[f]
			2.47 ± 0.22	245.4 ± 4.2	Experiment
Eu	$4f^74f^7\sigma_g{}^2\sigma_u{}^2$, ${}^{15}\sum_u{}^+$	4.878	0.080	27	SPP, ACPF[f]
		4.924	0.078	24	LPP,ACPF[g]
		4.887	0.102	26	LPP,CCSD(T)[g]
			0.30 ± 0.17	≈35[d]	Experiment
Gd	$4f^74f^7\sigma_g{}^2\sigma_u{}^1\pi_g{}^1\pi_u{}^2$, ${}^{19}\sum_g{}^-$	3.006	1.41	117	PP, ACPF [19]
			1.784 ± 0.35	138.7 ± 0.4	Experiment
Yb	$4f^{14}4f^{14}\sigma_g{}^2\sigma_u{}^2$, ${}^1\sum_g{}^+$	4.549	0.092	25	CCSD(T)[f]
		4.861	0.058	18	[20]
		4.19	0.17 ± 0.17	≈22[d]	Experiment
Lu	$4f^{14}4f^{14}\sigma_g{}^2\sigma_u{}^2\pi_u{}^2$, ${}^3\sum_g{}^-$	3.07 ± 0.03	1.40 ± 0.12	123 ± 1	This work
			1.43 ± 0.34	121.6 ± 0.8	Experiment

[a] The estimated experimental bond lengths for La_2 are from Ref. [9]

[b] Experimental values are from Ref. [8]. Spin-orbit corrections of −0.16 eV (La_2), −0.20 eV (Gd_2) and −0.30 eV (Lu_2) where added to the scalar-relativistic results

[c] The experimental values for La_2, Ce_2, Eu_2, Gd_2, Yb_2, and Lu_2 are from Refs. [6], [28], [22], [24], [22] and [7], respectively

[d] Estimated values

[e] For ACPF and CCSD(T) calculations, basis set superposition error is corrected using CPC

[f] Standard basis sets (14s13p10d8f6g)/[6s6p5d4f3g] augmented by a diffuse (3s3p3d3f3g) set

[g] Basis sets (10s9p8d7f7 g); $4f^7$ subconfiguration included in the PP core. Results correspond to a ${}^1\Sigma_g^+$ valence substate

this large discrepancy, but we want to point out that we also found a unbound $\sigma_g{}^2\pi_u{}^4\ {}^1\sum_g{}^+$ state for Lu_2 at the CCSD(T) level, both using large- and small-core pseudopotentials (Table 3). Moreover, for all levels of theory the calculated vibrational constants are substantially higher than the recently determined experimental value, whereas a reasonable agreement is observed for the $\sigma_g{}^2\sigma_u{}^2\pi_u{}^2\ {}^3\sum_g{}^-$ state.

In order to get a more complete picture of the electronic structure of lanthanide diatomics, we include unpublished results for the dimers of cerium, europium and ytterbium as well as published data for gadolinium [19] and ytterbium [20]. A selection of molecular constants (R_e, D_e, ω_e) from the latest and presumably most accurate theoretical calculations as well as corresponding experimental data or estimates are summarized in Table 4.

The elements La, Ce, Gd and Lu are the only lanthanides which possess a $4f^n5d^16s^2$ ($n = 0, 1, 7, 14$) ground-state configuration, whereas Eu and Yb have a $4f^{n+1}6s^2$ ($n = 6, 13$) ground-state configuration and exhibit the largest energy gap to the $4f^n5d^16s^2$ or $4f^{n+1}5d^26s^1$ configurations of all the lanthanide atoms [15]. Noting that both Ce and La have similar $5d^16s^2 \rightarrow 5d^26s^1$ promotion energies (Ce 0.29 eV, La 0.33 eV), one may expect the same ground-state valence configuration $\sigma_g{}^2\pi_u{}^4$. The low-lying states arising from all possible couplings between the open $4f$ shells of Ce_2 were tested, and a ${}^3\sum_u{}^+$ $[4f^1(\varphi_u{}^1)\ 4f^1(\varphi_g{}^1)\sigma_g{}^2\pi_u{}^4]$ ground state was obtained. Calculations for both Ce_2 and La_2 yield lower vibrational frequencies than the experimental values with similar deviations (Ce_2 58 cm^{-1}, La_2 53 cm^{-1}). The lower calculated binding energy for Ce_2 [CCSD(T) 2.06 eV] compared to the experimental value (2.47 ± 0.22 eV) is attributed mainly to the limited correlation method, cf. also La_2. Unfortunately, MRCI studies are not possible even for the ground state of Ce_2 because of the limitations of our current hardware capabilities. For Gd_2, a ground-state configuration with 18 unpaired electrons $(4f^74f^7\sigma_g{}^2\sigma_u{}^1\sigma_g{}^1\pi_u{}^2)$ was predicted theoretically [4] and later confirmed by experiment [21]. Recent calculations yield a ${}^{19}\sum_g{}^-$ ground state [19]. Therefore, the ground states of dimers composed of lanthanide elements with ground-state subconfiguration $5d^16s^2$ are most likely La_2 ${}^1\sum_g{}^+$ $\sigma_g{}^2\pi_u{}^4$, Ce_2 ${}^3\sum_u{}^+$ $4f^1(\varphi_u{}^1)4f^1(\varphi_g{}^1)\sigma_g{}^2\pi_u{}^4$, Gd_2 ${}^{19}\sum_g{}^-$ $4f^74f^7\sigma_g{}^2\sigma_u{}^1\sigma_g{}^1\pi_u{}^2$ and Lu_2 ${}^3\sum_g{}^-$ $4f^{14}4f^{14}\sigma_g{}^2\sigma_u{}^2\pi_u{}^2$. For La_2 and Ce_2, the analysis of the valence orbitals for the ground state indicates a weak contribution of the $4f$ shell to chemical bonding (Table 5); therefore, the $4f$ electrons should be treated as valence electrons in highly accurate calculations. For Lu_2, as expected as explained in the Introduction, relatively large contributions of the $6p$ shell to bonding are found (Table 5). From their binding energies, it is concluded that La_2 and Ce_2 exhibit stronger bonding than Gd_2 and Lu_2.

Table 5. Mulliken population analysis of the complete-active-space self-consistent-field wavefunction of La_2, Ce_2 and Lu_2 in their ground states. Contributions of atomic natural orbital basis functions corresponding to the atomic valence orbitals (La: 6*s*, 6*p*, 5*d*, 4*f*; Lu: 6*s*, 6*p*, 5*d*, 5*f*) are given in *parentheses* (%)

		s (6*s*)	*p* (6*p*)	*d* (5*d*)	f (4*f*, 5*f*)
La_2	σ_g	95 (93)	–	5 (5)	–
	π_u	–	1 (1)	96 (95)	3 (2)
Ce_2	σ_g	95 (93)	–	5 (5)	–
	π_u	–	2 (1)	95 (94)	3 (2)
Lu_2	σ_g	96 (96)	1 (1)	3 (3)	–
	σ_u	81 (80)	17 (10)	2 (2)	–
	π_u	–	31 (22)	69 (67)	–

For the $4f^7 4f^7 \sigma_g{}^2 \sigma_u{}^2\ {}^{15}\sum_u{}^+$ and $4f^{14} 4f^{14} \sigma_g{}^2 \sigma_u{}^2\ {}^1\sum_g{}^+$ ground states of Eu_2 and Yb_2, respectively, rather weak van der Waals bonding was found. Better agreement for the spectroscopic constants between our results and the available experimental data is obtained than in previous theoretical calculations [4, 20] (Table 4). We attribute this to the higher level of calculation in the present study. The derived binding energies of 0.08 eV for Eu_2 and 0.09 eV for Yb_2 are in reasonable agreement with the experimental values of 0.30(±0.17) eV and 0.17(±0.17) eV [8]. Since the potential curves have extremely shallow minima, the derived bond lengths (Eu_2 4.878 Å; Yb_2 4.549 Å) and vibrational frequencies (Eu_2 27 cm^{-1}, Yb_2 25 cm^{-1}) might be easily affected by errors. Nevertheless, the calculated vibrational frequencies agree quite well with estimates used in experimental work (Eu_2 35 cm^{-1}, Yb_2 22 cm^{-1})[22].

In order to test the reliability of pseudopotentials and basis sets for lanthanides, for the ground states of La_2, Eu_2 and Lu_2 large-core pseudopotentials [16, 23] (the number of core electrons for La, Eu and Lu is 46, 53 and 60, respectively) supplemented by a core polarization potential [20] accounting for both static and dynamic core polarization were also applied. These potentials yield similar spectroscopic constants as the small-core pseudopotentials, provided basis sets of similar quality are chosen (Tables 2, 3). The absolute deviations for bond lengths, binding energies and vibrational frequencies are at most 0.032 Å, 0.05 eV and 8 cm^{-1}, respectively. Previous CI calculations including single and double excitations and using these large-core pseudopotentials resulted in a ground-state assignment and spectroscopic constants in disagreement with both the current experimental and theoretical results, i.e., La_2 $\sigma_g{}^2 \sigma_u{}^1 \sigma_g{}^1 \pi_u{}^2\ {}^5\sum_u{}^-$ ($R_e = 3.25$ Å, $\omega_e = 130$ cm^{-1}, $D_e =$ 1.17 eV) or $\sigma_g{}^2 \pi_u{}^4\ {}^1\sum_g{}^+$ ($R_e = 2.830$ Å, $\omega_e = 167$ cm^{-1}, $D_e = 1.06$ eV) and Lu_2 $\sigma_g{}^2 \sigma_u{}^2 \sigma_g{}^2\ {}^1\sum_g{}^+$ ($R_e = 3.79$ Å, $\omega_e = 74$ cm^{-1}, $D_e = 0.55$ eV). Our present results demonstrate that this is mainly due to too limited one- and many-electron basis sets as well as possibly the fixing of the La 4*f* occupation to zero in the original parameterization [16].

The theoretical results for La_2, Ce_2, Eu_2, Gd_2, Yb_2 and Lu_2 summarized in Table 4 are in satisfactory overall agreement with the available experimental data. The ω_e values of La_2 and Ce_2 are a notable exception. In order to get some idea of possible matrix effects in the experimental work (Raman spectroscopy in an Ar matrix [6, 7]), we investigated a simple model system. A linear complex between a single Ar atom and La_2 as well as Lu_2 was geometry-optimized at the CCSD(T) level using large-core pseudopotentials for La and Lu [16, 20, 24] as well as Ar [25]. A (6s6p3d)/[4s4p3d] valence basis set was chosen for Ar [23]. Compared to the free La_2 (206 cm^{-1}) we found a substantially higher frequency (228 cm^{-1}) in the Ar–La_2 complex. In contrast to this, the Ar–Lu_2 complex exhibits a vibrational frequency (123 cm^{-1}) which is only slightly higher than for free Lu_2 (120 cm^{-1}).

Matrix shifts of vibrational frequencies with respect to gas-phase values are typically of the order of 0–3%, but a few exceptions exist (XeF gas phase 204 cm^{-1}, Ne matrix 227 cm^{-1}) [26, 27]. As noted by Liu et al. [6] the force constant derived from Raman spectroscopy in an Ar matrix is anomalously large. Although our simple model does not fully explain the disagreement in ω_e of approximately 50 cm^{-1} for La_2, it indicates that La_2 could be significantly affected by Ar matrix effects, whereas Lu_2 behaves quite normally. We attribute this different behavior mainly to the absence/presence of an occupied σ_u orbital (strongly polarized away from the bond) in La_2/Lu_2 (Table 5), i.e., whereas the Pauli repulsion between Ar $3p^6$ and Lu_2 $\sigma_u{}^2$ allows only a very weak interaction in Ar–Lu_2 (distance 4.9 Å, force constant 4×10^{-4} au), the "electron deficiency" due to the unoccupied La_2 σ_u leads to a more stable Ar–La_2 complex (distance 3.3 Å, force constant 6×10^{-3} au). Further experimental work, i.e., measurements in a less polarizable Ne matrix, could help to understand the high ω_e of La_2 and Ce_2.

4 Conclusion

Gaussian (14s13p10d8f6g)/[6s6p5d4f3g] atomic natural orbital valence basis sets for relativistic energy-consistent small-core lanthanide pseudopotentials were used to establish the ground states for the La_2 (${}^1\sum_g{}^+$ $\sigma_g{}^2 \pi_u{}^4$), and Lu_2 (${}^3\sum_g{}^-$ $4f^{14} 4f^{14} \sigma_g{}^2 \sigma_u{}^2 \sigma_u{}^2$) dimers and to derive the spectroscopic constants. The molecular parameters (La_2: $R_e = 2.70 \pm 0.03$ Å, $D_e = 2.31 \pm 0.13$ eV, $\omega_e = 186 \pm 13$ cm^{-1}; Lu_2: $R_e = 3.07 \pm 0.03$ Å, $D_e = 1.40 \pm 0.12$ eV, $\omega_e = 123 \pm 1$ cm^{-1}) derived on the basis of MRCI and coupled-cluster calculations, including corrections for the atomic fine structure and basis set superposition errors, are in satisfactory agreement with experimental data (La_2: $D_e = 2.52 \pm 0.22$ eV, $\omega_e = 236 \pm 0.8$ cm^{-1}; Lu_2: $D_e = 1.43 \pm 0.34$ eV, $\omega_e = 122 \pm 1$ cm^{-1}), except for the La_2 vibrational frequency. Model calculations point to possible large positive matrix shifts of ω_e for La_2, but normal behavior for Lu_2. The same ground-state valence configuration as for La_2 is obtained for Ce_2 [${}^3\sum_u{}^+$, $4f^1(\varphi_u{}^1) 4f^1(\varphi_g{}^1) \sigma_g{}^2 \pi_u{}^4$]. By comparing the calculated results for all dimers (La_2, Ce_2, Gd_2, Lu_2) composed of lanthanide elements with the ground state-subconfiguration $5d^1 6s^2$, it is concluded that La_2 and Ce_2 exhibit stronger bonding than Gd_2 and Lu_2. Weak contributions to chemical bonding of 4*f* orbitals (3%) are found for La_2 and Ce_2, whereas for Lu_2 a relatively large contribution from the 6*p* orbital (32%) is detected. Calculations using both large-core and small-core pseudopotentials give similar spectroscopic constants for La_2, Eu_2 and Lu_2, indicating that both pseudopotentials are reliable.

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