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A combination of quasirelativistic pseudopotential and ligand field calculations for lanthanoid compounds

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Summary. Improved energy-adjusted quasirelativistic pseudopotentials for lanthanoid atoms with fixed valency are presented and tested in molecular calculations for CeO, CeF, EuO, GdO, YbO, and YbF. The pseudopotential calculations treat the lanthanoid 4*f* shell as part of the core and yield accurate estimates for average bond lengths, vibrational frequencies and dissociation energies of all states belonging to a superconfiguration. Information for each individual state of the considered superconfiguration may be obtained from subsequent ligand field model calculations. The results of this combined pseudopotential and ligand field approach (PPLFT) are compared to more accurate calculations with ab initio pseudopotentials that include the lanthanoid 4*f* orbitals explicitly in the valence shell and to available experimental data.

Key words: Lanthanoid elements – Pseudopotentials – Ligand field model

1 Introduction

In two previous papers [1, 2] we presented two sets of quasirelativistic energy-adjusted pseudopotentials for the rare earth elements La through Lu. The first set of pseudopotentials treats the chemically rather inactive lanthanoid 4*f* shell as part of the core. Separate pseudopotentials have been adjusted for integral 4*f* occupation numbers each corresponding to a specific valency of the atom in a molecular environment. The pseudopotentials are useful to obtain average molecular constants for all states characterized by a 4*f* occupation number on the lanthanoid center and a valence substate [3, 4], i.e. for all states belonging to a so-called superconfiguration [5]. The second set of pseudopotentials treats the lanthanoid 4*f* orbitals explicitly in the valence shell and allows any valency of the rare earth element in molecules, at a considerable higher computational effort, however.

In a number of studies on heteronuclear diatomic molecules (CeO [6], EuO [7], GdO [8], YbH and YbF [9], and YbO [10]) we compared the results obtained from both pseudopotential schemes with experimental results. Whereas the agreement of the results obtained from the second set of pseudopotentials with experimental data was usually excellent, the use of the first set of pseudopotentials led to some systematic errors, especially at the beginning of the rare earth series. In case of CeO we obtained $R_e = 1.821$ Å, $D_e = 7.16$ eV, $\omega_e = 835\ \mathrm{cm}^{-1}$ [6] from configuration interaction calculations including the Langhoff–Davidson size consistency correction [11] (CISD + Q) for the average of all 16 Ω-states arising from the $4f^1\sigma^2\sigma^2\pi^4\sigma^1$ superconfiguration when the $4f$ orbitals were explicitly treated in the valence space. The corresponding state-averaged experimental values are $R_e = 1.811$ Å, $D_e = 7.94$ eV, $\omega = 823\ \mathrm{cm}^{-1}$ [12]. For the pseudopotential modelling a trivalent Ce atom with a fixed $4f^1$ subconfiguration somewhat larger errors occurred, especially for the bond length and the dissociation energy, i.e. $R_e = 1.926$ Å, $D_e = 6.34$ eV, $\omega_e = 823\ \mathrm{cm}^{-1}$ [6]. The too long bond distance and the too small dissociation energy may be partly attributed to a nonnegligible participation of the Ce $4f$ orbitals in chemical bonding which is only fully accounted for when the $4f$ orbitals are explicitly included in the calculation. Towards the end of the row the lanthanoid $4f$ orbitals become more core-like (cf. the lower one-particle energies and the smaller $\langle r \rangle$-expectation values) and their contribution to chemical bonding becomes negligible.

In this contribution we improve and extend our first pseudopotential scheme in the following two aspects: a modification of the f part of the pseudopotential allows for $4f$ orbital contribution in bonding and brings the results into better agreement with those obtained with the second set of pseudopotentials and with available experimental data; a combination of pseudopotential calculations for a specific superconfiguration with subsequent ligand field model calculations for all individual states resulting from this superconfiguration is proposed and extends our quantum chemical treatment of rare earth compounds following an electronic structure model proposed by Field [5] for rare earth monoxides, i.e. a treatment of the valence space by molecular orbital methods and of the core space by ligand field theory. This combination of improved pseudopotential and ligand field calculations (PPLFT) is applied to selected diatomics of the lanthanoid elements, i.e. CeO, CeF, EuO, GdO, YbF, and YbO. The results are compared to experimental data and to ab initio pseudopotential calculations that treat the $4f$ orbitals explicitly in the valence space. Our PPLFT approach is an alternative to recently published semiempirical intermediate neglect of differential overlap calculations with adaption to spectroscopy (INDO/S) [13, 14]. In contrast to this approach we do not need to derive the parameters used in our scheme from experimental atomic or molecular data.

2 Method

The valence model Hamiltonian (in atomic units) used in this work is:

$$H = -\tfrac{1}{2}\sum_i \Delta_i + \sum_{i,\lambda} V_\lambda(r_i) + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{\lambda<\mu} \frac{Q_\lambda Q_\mu}{R_{\lambda\mu}}$$

where $V_\lambda(r_i)$ is a semilocal pseudopotential for core λ:

$$V_\lambda(r_i) = -\frac{Q_\lambda}{r_{\lambda i}} + \sum_l \sum_k A_{\lambda kl} \exp(-a_{\lambda kl} r_{\lambda i}^2) P_{\lambda l}$$

i and j are electron indices, λ and μ are core indices; Q_λ denotes the charge of the core λ and $P_{\lambda l}$ is the projection operator onto the Hilbert subspace of core λ with angular symmetry l:

$$P_{\lambda l} = \sum_{m_l} |lm_l\rangle\langle lm_l|.$$

In case of the pseudopotentials that treat the $4f$ orbitals explicitly in the valence shell the Hamiltonian was augmented by a spin-orbit operator [2].

As described in detail in [1] and [2] our pseudopotentials have been adjusted to valence energies derived from atomic quasirelativistic ab initio calculations. For the pseudopotentials that model rare earth elements of a specific valency [1] we adjusted the f part to guarantee a fixed integral $4f$ occupation number. In order to allow for some participation of the $4f$ orbitals in chemical bonding we now loosen this restriction in the following way: the s, p, and d part of the pseudopotential is the same as in [1]; the coefficient of the f part of the pseudopotential is adjusted to the valence energy of Ln $(1s^1 \ldots 4f^n)4f^1 5s^2 5p^6 6s^2$ with respect to a Ln^{11+} $(1s^2 \ldots 4f^n)$ core for trivalent rare earth atoms and to the valence energy of Ln $(1s^2 \ldots 4f^{n+1})4f^1 5s^2 5p^6 6s^1$ with respect to a Ln^{10+} $(1s^2 \ldots 4f^{n+1})$ core for divalent rare earth atoms (The core-valence separation chosen in the pseudopotential calculations is indicated by parenthesis). The exponents have been derived by linear interpolation of values for trivalent Ce and Yb and divalent La and Tm, which were obtained by adjustment to the valence energies of Ln^{2+} $(1s^2 \ldots 4f^n)4f^1 5s^2 5p^6$, $(1s^2 \ldots 4f^n)5s^2 5p^6 5f^1$ and Ln^{+} $(1s^2 \ldots 4f^{n+1})4f^1 5s^2 5p^6$, $(1s^2 \ldots 4f^{n+1})5s^2 5p^6 5f^1$ for the trivalent and divalent case, respectively. In the spirit of the superconfiguration concept only an average coupling within the $4f$ shell and between the $4f$ shell and other open shells was taken into account. In contrast to our earlier work the f parts of the pseudopotentials are now designed to describe better partial occupations of the $4f$ shell due to some mixing of the $4f$ orbitals into the molecular orbitals, i.e. the $4f$ occupation numbers q modelled with the pseudopotentials might be $n \leqslant q < n + 1$ for trivalent or $n + 1 \leqslant q < n + 2$ for divalent lanthanide atoms in molecules. Preferably the modelled $4f$ occupation number q should be close to the number of $4f$ electrons included in the pseudopotential core. We note, that it should not be attempted to occupy the $4f$ orbitals explicitly in the calculations with the pseudopotentials presented here, e.g. instead of calculating a molecule with an (approximate) $4f^{n+1}$ subconfiguration on the rare earth center with a pseudopotential modelling a $4f^n$ core and explicitly occupying the $4f$ shell with one electron, one should rather use the pseudopotential modelling the $4f^{n+1}$ core. The modified f parts of the pseudopotentials are summarized in Table 1.

The pseudopotential calculations described above have been combined with crystal field model calculations in order to obtain information on individual states belonging to a superconfiguration. The model Hamiltonian may be written as a sum of a Hamiltonian for a free rare earth ion and a ligand field Hamiltonian:

$$H = H_{FI} + H_{LFT}.$$

The Hamiltonian matrix is built with the free ion wavefunctions which were obtained from quasirelativistic numerical Hartree–Fock calculations within the Wood–Boring scheme[15]. Since we are interested in relative energies only, it suffices to consider the open shell orbitals, i.e. the $4f$ and $6s$ orbitals on the lanthanoid center. All terms that only cause energetic shifts of all states belonging to a superconfigurtion will be omitted in the following. The energetic splittings arising from the free ion Hamiltonian are determined by the exchange integral $G^3(4f, 6s)$ and the spin-orbit parameter $\zeta(4f)$. In order to keep our model simple for the diatomic systems studied here we do not include the $5d$ and $6p$ orbitals in the calculations. As will be outlined below this neglect is overcome by treating the exchange integral $G^3(4f, 6s)$ as an adjustable parameter for the

Table 1. Modified f part for the quasirelativistic pseudopotentials from [1]

Ln	$Q = 10$ A_3	a_3	$Q = 11$ A_3	a_3
La	−36.379554	3.7909	−36.010015	4.0286
Ce	−40.325835	4.0265	−40.585328	4.2785
Pr	−44.509732	4.2761	−46.078536	4.6000
Nd	−48.922550	4.5382	−51.581518	4.9206
Pm	−53.570506	4.8126	−57.138239	5.2417
Sm	−58.460194	5.0994	−62.736825	5.5627
Eu	−63.601050	5.3988	−68.468426	5.8838
Gd	−69.000952	5.7110	−74.248790	6.2049
Tb	−74.670692	6.0363	−80.073275	6.5259
Dy	−80.624580	6.3755	−85.930099	6.8470
Ho	−86.873762	6.7288	−91.830614	7.1680
Er	−93.433748	7.0972	−97.773598	7.4891
Tm	−100.318575	7.4810	−103.731072	7.8101
Yb	7.016510	1.3864	−109.747695	8.1312

interaction between a core-like $4f$ shell and a valence orbital of σ-symmetry with predominantly $6s$ character. The ligand field part of the model Hamiltonian may be written as:

$$H_{LFT} = \sum_{i,l,m} (B^l_m)_i (C^l_m)_i$$

where i is an electron index as before. The C^m_l are spherical irreducible tensor operators and may be written in terms of the spherical harmonics Y_{lm}:

$$C^l_m = \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{lm}(\theta, \phi).$$

For the diatomic molecules considered here the $C_{\infty v}$ point group permits only contributions of the axial components with $m = 0$ to the crystal field splittings. Energy splittings are caused by the corresponding matrix elements built with the $4f$ orbitals on the rare earth center. In case of a ligand represented by a point charge, e.g. $Q = -1, -2$ for F and O, respectively, the parameters B^l_m may be obtained from the radial numerical atomic orbitals R_{4f} [15] of the rare earth ion according to:

$$B^l_0(4f) = Q \int_0^\infty \frac{r^l_<}{r^{l+1}_>} R^2_{4f}(r)\, dr$$

with $l = 0, 2, 4, 6$; $r_<$ and $r_>$ denote the smaller and larger value of r and the rare-earth ligand distance, respectively.

In this contribution we show that the results of ligand field model calculations may be considerably improved when the parameters G^3 and B^l_0 are determined from a molecular pseudopotential calculation for the considered superconfiguration instead of an atomic all-electron calculation for the free ion. We choose the cerium diatomics CeO and CeF for our test calculations for the following reason: at the beginning of the lanthanide series the $4f$ orbitals are still relatively diffuse and a simple point charge approximation for an O^{2-} or a F^- ligand is bound to fail, i.e. these molecules will probably yield the worst results for our approach. Results for the less critical molecules YbH, YbO, and YbF will be presented elsewhere [9, 10]. In order to be able to predict energy splittings between states for experimentally not well investigated molecules we avoid to adjust the parameters of our model Hamiltonian to experimental data as usually done in ligand field calculations.

Instead of taking the ligand field parameters B_0^l from quasirelativistic all-electron calculations Ce^{n+}, we derived them from the matrix elements $\langle 4f, m|V|4f, m\rangle$ ($m = 0, \pm 1, \pm 2, \pm 3$), which were calculated by a numerical integration using the electrostatic potential V from pseudopotential calculations including the $4f$ orbitals in the core and radial parts of the quasirelativistic $4f$ all-electron orbitals of Ce^{n+} ($n = 1$ for CeF, $n = 2$ for CeO). The inclusion of exchange interaction by means of Slater's local exchange potential led only to minor changes in the derived values.

CeO has a $4f^1\sigma^1$ ground state superconfiguration [5, 12]. It has been shown in quasirelativistic ab initio pseudopotential calculations including the $4f$ orbitals in the valence space [6] that the Ce $4f$ shell is rather atomic like, whereas the singly occupied σ orbital is a hybrid with 82% Ce $6s$ and 16% Ce $6p$ contributions and is polarized away from the oxygen ligand. The $G^3(4f, 6s)$ exchange integral used as a parameter in ligand field model calculations is therefore considerably reduced from its free ion value. In order to derive the reduced averaged singlet-triplet splitting from molecular calculations we adjusted spin-dependent Ce pseudopotentials for singlet and triplet coupling of a single electron in a s, p, d, or f orbital to the $4f^1$ core. The corresponding difference potential:

$$\Delta V_\lambda = \sum_l \sum_k \Delta A_{\lambda kl} \exp(-a_{\lambda kl} r_{\lambda i}^2) P_{\lambda l}$$

was applied for every considered bond distance in first order perturbation theory to the CeO valence subconfiguration. The calculated averaged singlet-triplet splitting was used to determine the effective G^3 exchange integral for the ligand field calculations. The parameters of the difference potential are summarized in Table 2.

Due to the core-like character of the $4f$ orbitals the spin-orbit parameter ζ_{4f} changes only slightly when going from the atom to the molecule. We therefore used the quasirelativistic all-electron values for Ce^+ and Ce^{2+} for CeF and CeO, respectively.

Table 2. Difference potential for the singlet-triplet splitting in cerium (III) compounds with a Ce $4f^1$ subconfiguration

l	k	ΔA_{kl}	a_{kl}
0	1	3.121663	3.5222
	2	−0.122956	1.7611
1	1	2.580684	3.0177
	2	−0.036640	1.5089
2	1	3.989912	2.1443
	2	0.020886	1.0722
3	1	10.622089	4.2785

All calculations neglecting spin-orbit coupling have been carried out with the MOLPRO program system [16] in C_{2v} symmetry. For the calculations that include the $4f$ orbitals in the core we applied the energy-optimized $(7s6p5d)/[5s4p3d]$ basis sets from [1] and added four f functions from the all-electron basis sets of [17]. The calculations of CeF with an explicit treatment of the $4f$ orbitals used the Ce pseudopotential from [2] together with the $(12s11p9d8f)/[9s8p6d5f]$ Ce basis set already applied in similar calculations on CeO [6]. The CeF results that account for spin-orbit coupling were obtained with a smaller $(10s7p7d4f)/[8s5p5d3f]$ Ce basis set, the spin-orbit operators and the CIPSI/CIPSO program system [18] as described for CeO in [6]. For O and F we used the $(9s5p)/[4s2p]$ basis set by Dunning [19] together with his diffuse p function [20] and added a d function[20] yielding a $(9s6p1d)/[4s3p1d]$ basis set.

3 Results

The results of our pseudopotential calculations on low-lying superconfigurations of selected lanthanoid diatomics are summarized in Table 3. For comparison we also list the corresponding values obtained in pseudopotential calculations with an explicit treatment of the $4f$ orbitals (c.f. refs. [6] (CeO), [7] (EuO), [8] (GdO), [10] (YbO), [9] (YbF), and this work (CeF)) and experimental values. Compared to our earlier calculations[1] a considerable improvement is observed for the bond lengths at the beginning of the $4f$ series, e.g. the equilibrium distance of CeO in its $4f^1\sigma^1$ ground state superconfiguration is now 1.819 Å at the CISD + Q level in excellent agreement with the experimental value of 1.820 Å; the best value from [6] is 1.926 Å. Similarly, the dissociation energies are somewhat improved (CeO: 6.34 eV [6], 7.25 eV this work), whereas the vibrational constants remain almost unaltered (CeO 822 cm^{-1} [6], 834 cm^{-1} this work). The differences in the results between the simple pseudopotential calculations treating the $4f$ orbitals as part of the core and those including them explicitly in the valence space are now relatively small. Thus, the modification of the f part of our pseudopotentials, i.e. relaxing somewhat the constraint of a chemical inert $4f$ shell, leads to an overall improvement of the results.

The energetic splitting of the electronic states arising from the $4f^1\sigma^1$ superconfiguration of CeO are summarized in Table 4. The PPLFT approach proposed in this contribution yields values in reasonable agreement with the results of previous work treating the $4f$ orbitals explicitly[6] as well as with available experimental data [12]. The relative ordering of the states is determined by the three ligand field parameters B_0^l ($l = 2, 4, 6$), the exchange integral $G^3(4f, 6s)$ and the spin-orbit parameter ζ_{4f}. When these parameters are taken from quasirelativistic all-electron calculations of the Ce^{2+} ion ($B_0^2 = 14644\ \mathrm{cm}^{-1}$, $B_0^4 = 3647\ \mathrm{cm}^{-1}$, $B_0^6 = 1566\ \mathrm{cm}^{-1}$, $G^3 = 2867\ \mathrm{cm}^{-1}$, $\zeta_{4f} = 693\ \mathrm{cm}^{-1}$ for a bond distance of 3.4 a.u.), i.e. taking a $\mathrm{Ce}^{2+}\mathrm{O}^{2-}$ charge distribution underlying the ligand field model [5] seriously, rather poor results are obtained: the experimentally observed Ω states corresponding to the Ce^{2+} $(4f^16s^1\,{}^2F_J)$ O^{2-} ($J = 5/2$ and $7/2$) limit of the separated ions are spread over an energy interval from 0 cm^{-1} to 1932 cm^{-1} and from 2040 cm^{-1} to 4458 cm^{-1}, respectively; the corresponding values obtained with the point charge ligand model are 0 cm^{-1} to 8116 cm^{-1} and 2077 cm^{-1} to 11,267 cm^{-1}, respectively. Due to the core-like character of the $4f$ orbitals the free ion value of the spin-orbit parameter ζ_{4f} leads to reasonable agreement of the calculated energy separation between the two manifolds

Table 3. Spectroscopic constants of selected lanthanoid diatomics in comparison to experimental values (first line: 4*f* orbitals included in the pseudopotential core; second line: 4*f* orbitals treated explicitly in the valence space)

LnX	4*f*	R_e (Å)			D_e (eV)			ω_e (cm^{-1})		
		SCF	CISD + Q	exp.	SCF	CISD + Q	exp.	SCF	CISD + Q	exp.
CeO	1	1.799	1.189	1.820	5.00	7.25	8.22	861	834	824
		1.808	1.827		5.25	7.28		870	838	
CeF	1	2.046	2.035	2.048	4.97	6.46		560	571	
		2.043	2.030		5.01	6.13		566	576	
EuO	6	1.783	1.802		2.04	3.11	4.28	848	819	~830
		1.798	1.814		1.82	3.88		884	853	
	7	1.890	1.912	~1.89	0.94	3.22	4.88	680	644	688
		1.905	1.919		1.20	3.92		725	702	
GdO	7	1.783	1.801	1.812	4.24	6.62	7.39	848	820	824
		1.803	1.822		3.79	6.37		879	845	
YbO	13	1.780	1.796		3.43	3.22	4.01	865	822	~830
		1.791	1.768		3.42	3.05		899	907	
	14	1.902	1.933	1.807	−0.12	2.33	4.12	700	620	699
		1.903	1.886		−0.15	2.53		713	699	
YbF	14	2.092	2.093	2.016	3.74	4.63	4.89	468	457	502
		2.071	2.045		3.91	4.90		481	492	

Table 4. Spectroscopic constants (cm^{-1}) for CeO

No	Ω	T_0	T_e		$\Delta G_{1/2}$	ω_e		B_0	B_e	
		exp.	a	b	exp.	a	b	exp.	a	b
1	$X_1 2$	0	0	0	824	837	828	0.3545	0.3519	0.3496
2	$X_2 3$	80	119	101	823	836	828	0.3569	0.3520	0.3496
3	$W_1 1$	812	913	923		838	823	0.361	0.3546	0.3543
4	$W_2 2$	912	1045	968	823	838	832	0.3614	0.3548	0.3539
5	$V_1 0^-$	1679	1396	1589		831	819	0.3579	0.3549	0.3614
6	$V_2 1$	1870	1476	1679		828	838	0.343	0.3542	0.3620
7	$U_1 0^+$	1932	1715	1769		835	820	0.377	0.3546	0.3607
8	$X_3 4$	2040	2139	2302	822	838	828	0.3533	0.3518	0.3492
9	$X_4 3$	2141	2286	2487	824	837	829	0.3566	0.3519	0.3495
10	$W_3 3$	2617	2872	3086	825	841	833	0.356	0.3550	0.3532
11	$W_4 2$	2772	3039	3165	823	839	833	0.3600	0.3551	0.3532
12	$V_3 2$	3463	3386	3771	821	836	834	0.355	0.3554	0.3562
13	$V_4 1$	3642	3391	3766		828	834		0.3552	0.3596
14	$T_1 0^-$	3822	3476	4120		836	843	0.375	0.3559	0.3597
15	$U_2 1$	4133	3605	4249		843	847		0.3541	0.3566
16	$U_3 0^+$	4458	4234	4314		837	843	0.367	0.3558	0.3595

[exp] experimental values from [12]
[a] calculation with explicit treatment of the $4f$ orbitals
[b] calculation with $4f$ orbitals in the pseudopotential core

($2077\,\mathrm{cm}^{-1}$) with the experimental value ($2040\,\mathrm{cm}^{-1}$). The average absolute value of the matrix elements $\langle 4f, m|V|4f, m\rangle$ equals B_0^0. When derived by numerical integration using the electrostatic potential from pseudopotential calculations for the valence subconfiguration and atomic all-electron $4f$ orbitals it corresponds to a point charge $Q = -2.07$ of the ligand (at a bond distance of 3.4 a.u.). This result would support the $\mathrm{Ce}^{2+}\mathrm{O}^{2-}$ point charge model, however, the energetic splitting between the matrix elements derived from molecular pseudopotential calculations is considerably smaller than when obtained from atomic all-electron B_0^l values. Since the differences betwen these matrix elements, which determine the ligand field parameters B_0^l ($l = 2, 4, 6$), are less than 1% of their absolute value, small numerical inaccuracies in the integration scheme lead to significant errors in the final result. In addition, errors introduced by the nonorthogonality of the $4f$ all-electron orbitals and the valence pseudoorbitals would not be accounted for. We therefore fixed the ratio of the B_0^l parameters to the atomic all-electron results and determined only the dominant parameter B_0^2, which is least affected by the above-mentioned sources of errors, from the calculated matrix elements ($B_0^2 = 6140\,\mathrm{cm}^{-1}$, $B_0^4 = 1540\,\mathrm{cm}^{-1}$, $B_0^6 = 656\,\mathrm{cm}^{-1}$ for a bond distance of 3.4 a.u.). From the singlet-triplet splitting of $375\,\mathrm{cm}^{-1}$ (at a bond distance of 3.4 a.u.) an effective $G^3(4f, 6s)$ integral of $1313\,\mathrm{cm}^{-1}$ is derived. The coupling between the $4f$ core orbitals and the s symmetrical part of the singly occupied valence orbital contributes with 75% to this value.

For the $4f^1\sigma^2$ superconfiguration of CeF we performed quasirelativistic pseudopotential configuration interaction calculations including the $4f$ orbitals explicitly in the valence shell and accounting for spin-orbit coupling. The results of these calculations, which were carried out similar to previous work on CeO [6], are listed in Table 5. The calculated rotational constants of the

Table 5. Spectroscopic constants (cm^{-1}) for CeF

No		T_e		ω_e		B_e	
	Ω	a	b	a	b	a	b
1	5/2	0	0	579	571	0.2434	0.2418
2	3/2	807	999	583	567	0.2455	0.2436
3	1/2	1445	1757	598	566	0.2457	0.2464
4	7/2	2191	2327	577	572	0.2431	0.2417
5	5/2	2867	3150	577	568	0.2450	0.2432
6	3/2	3327	3840	600	567	0.2461	0.2441
7	1/2	3834	4280	574	565	0.2440	0.2473

[exp] experimental value for the rotational constant of the ground state $B_e = 0.2403\ \mathrm{cm}^{-1}$ from [21]

[a] calculation with explicit treatment of the $4f$ orbitals

[b] calculation with $4f$ orbitals in the pseudopotential core

$\Omega = 5/2$ ground state ($4f$ orbitals in core space: $B_e = 0.2418\ \mathrm{cm}^{-1}$; $4f$ orbitals in valence space: $B_e = 0.2434\ \mathrm{cm}^{-1}$) agree well with the corresponding experimental value ($B_e = 0.2403\ \mathrm{cm}^{-1}$; [21]). No other experimental values are known to our knowledge. The energetic splitting of the ground-state configuration into seven Ω states is determined by the three ligand field parameters B_0^l ($l = 2, 4, 6$) and the spin-orbit parameter ζ_{4f} in the PPLFT calculations. The parameters were derived as described before for CeO ($B_0^2 = 3324\ \mathrm{cm}^{-1}$, $B_0^4 = 686\ \mathrm{cm}^{-1}$, $B_0^6 = 255\ \mathrm{cm}^{-1}$ for a bond distance of 3.85 a.u.). The agreement between the PPLFT results and the pseudopotential calculations with an explicit treatment of the $4f$ orbitals is excellent for vibrational and rotational constants and quite reasonable for the term energies, c.f. Table 5. When the ligand field parameters are derived from a quasirelativistic all-electron calculation for the Ce^+ ion the energy levels are spread over an energy interval of approximately $5200\ \mathrm{cm}^{-1}$ in contrast to $3800\ \mathrm{cm}^{-1}$ derived from pseudopotential calculations with an explicit treatment of the $4f$ orbitals or $4300\ \mathrm{cm}^{-1}$ obtained in PPLFT calculations, when the parameters are derived from the ligand field potential of the molecular calculation.

We like to point out that the results of the PPLFT approach proposed here could be considerably improved when parameters of the model Hamiltonian are adjusted to experimental molecular data if available. Such semiempirical calculations could be carried out for the well investigated CeO, but not for CeF, where the necessary information is missing. We note that, due to an increase of the core character of the $4f$ shell, at the end of the $4f$ row, the use of free ion values in the ligand field model Hamiltonian leads to quite satisfactory results (cf. [10] for YbO and [9] for YbH and YbF). From an economical point of view the PPLFT approach discussed here is a rather efficient method for the treatment of rare earth compounds: the pseudopotential SCF calculation for the considered superconfiguration can be run in a few minutes on a workstation and the subsequent ligand field model calculation requires only a few seconds on a personal computer. A time-consuming step for larger molecules is probably the pointwise calculation of the electrostatic potential used to determine the ligand field parameters. Considerable computational savings with only little loss of accuracy for bond lengths and vibrational constants can be achieved by the neglect of f basis functions on the rare earth atom. An extension of the approach to other than diatomic molecules appears to be worthwhile.

4 Conclusion

A simple modification of the *f* part of previously published pseudopotentials for lanthanoid elements with a fixed valency has been shown to bring the results of molecular calculations into excellent agreement with averaged values from corresponding calculations with an explicit treatment of the 4*f* shell as well as available experimental data. The pseudopotential calculations for superconfigurations were combined with subsequent ligand field model calculations in order to obtain information on spectroscopic constants of individual electronic states belonging to the considered superconfiguration.

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