Pseudopotential study of the rare earth monohydrides, monoxides and monofluorides

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Nonrelativistic and quasirelativistic energy-adjusted pseudopotentials for fixed $4f$ subconfigurations of the rare earth elements La through Lu together with corresponding optimized valence basis sets have been used in SCF and CI(SD) calculations to determine the spectroscopic constants for the energetically low lying superconfigurations of the lanthanide monohydrides, monoxides and monofluorides. The experimentally observed trends in dissociation energies, bond lengths and vibrational frequencies for the ground states of the calculated superconfigurations of the monoxides and monofluorides are well reproduced. The results for the monohydrides are mainly predictions.

Key words: Pseudopotentials—Rare earth elements

1. Introduction

In a previous paper [1] we presented nonrelativistic and quasirelativistic pseudopotentials and the corresponding optimized valence basis sets for the rare earth elements La through Lu. We adjusted our pseudopotentials for fixed $4f$ subconfigurations, corresponding to the cases of trivalent ($4f^n$ occupation) and divalent ($4f^{n+1}$ occupation) rare earth atoms ($n = 0$–14 for La–Lu), by attributing the partially occupied $4f$ orbitals to the (open shell) core and treating only the $5s$, $5p$, $5d$ and $6s$ orbitals explicitly in the valence shell. This choice of the core has the advantage that the chemically very similar rare earth elements can be treated on equal footing. This is something that is usually advocated for pseudopotentials of elements belonging to the same group in the periodic system.

Moreover it exploits the well-known fact that the rare earth elements are usually trivalent and less frequently bivalent (or tetravalent) in their compounds. Our approach mainly follows the ideas developed by Field [2], who pointed out that up to several thousand low lying electronic states of the rare earth monoxides resulting from a given atomic-like $4f$ subconfiguration and a corresponding valence subconfiguration have very similar spectroscopic constants and may be combined to form a so-called superconfiguration. Calculations using the derived pseudopotentials yield approximate spectroscopic constants for all electronic states arising from a single superconfiguration. The corresponding $4f$ subconfiguration is determined by the choice of the pseudopotential, whereas the valence subconfiguration is treated explicitly in the SCF (self consistent field) and CI(SD) (configuration interaction with single and double excitations) calculations. The method is purely *ab initio* when only atomic and molecular states within a given $4f$ subconfiguration are considered. Moreover, for the ground states of La, Yb and Lu the core is a closed shell system and the corresponding pseudopotentials should be of the same quality as those derived previously for transition metals [3]. In order to estimate the energy separations of atomic or molecular states of superconfigurations with different $4f$ subconfigurations, we calculate the energy differences between them and the atomic valence subconfigurations that correspond to the lowest experimental states of each $4f$ subconfiguration. The energy separations between the latter can be taken either from all-electron calculations or from experiment. In view of the large correlation errors exhibited by nonrelativistic Hartree–Fock (HF) or quasirelativistic Wood–Boring (WB) all-electron calculations [1], we prefer to use experimental atomic data [4] for correcting our pseudopotential CI(SD) results to compare them with experiment. This empirical correction only affects some excitation, ionization and dissociation energies, and does not affect bond lengths or vibrational frequencies. In order to compare our results with those derived from all-electron or pseudopotential calculations where the $4f$ orbitals are included in the valence space one may use the HF or WB energy differences of the reference states given in [1].

In this paper we present a pseudopotential study of the lanthanide monohydrides, monofluorides and monoxides in order to test the quality of our approach in molecular calculations. Since to our knowledge no theoretical work for these compounds has appeared in the literature (an effective core potential calculation on NdO was mentioned in [5], however no details have been reported) we only compare our results to available experimental data. Pseudopotentials for all rare earth elements based on the density functional approach [6], effective core potentials for La [7, 8] and model potentials for Lu [9, 10] have been published in literature, however no molecular tests have been performed.

2. Method

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

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

where $V_\lambda(r_{i\lambda})$ is a semilocal pseudopotential of the form

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

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

i and j are electron indices whereas 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 angular symmetry l with respect to the core λ.

As described in detail in [1] we adjusted the parameters A_{kl} and a_{kl} for pseudopotentials representing respectively the cores of trivalent and divalent rare earth elements, to both nonrelativistic and quasirelativistic atomic excitation and ionization energies.

2.1. Nonrelativistic pseudopotentials

In a first step the parameters A_{kl} and a_{kl} ($k = 1, 2$ for $l = 0, 1, 2$; $k = 1$ for $l = 3$) were separately obtained for each value of the quantum number l in a single electron fit (SEFIT [11]) to the HF (Hartree Fock)-valence energies [12] of the $Ln^{(Q-1)+}1s^2\ldots4f^m\,nl^1\,{}^2L$ valence substates of the one-valence electron ions ($n = 5\text{-}8$; $l = s, p, d, f$; $L = S, P, D, F$; trivalent rare earth: $Q = 11$ and $m = 0$ for La through $m = 14$ for Lu; divalent rare earth: $Q = 10$ and $m = 1$ for La through $m = 14$ for Yb; for the $4f$-orbitals only an average coupling [13] was taken into account).

In a second step the coefficients A_{kl} ($l = 0, 1, 2$) were improved in a multi electron fit (MEFIT [14]) by adjusting them in a least-squares fit to the HF-valence energies [12] of 8 (divalent) or 10 (trivalent) low-lying valence substates of Ln and Ln$^+$. The f-pseudopotential was not modified in this step and by means of its adjustment to the valence energies of the $5f^1$ and $6f^1\,{}^2F$ valence substates is designed to guarantee a fixed $4f$-occupancy.

2.2. Quasirelativistic pseudopotentials

All exponents a_{kl} of the quasirelativistic pseudopotentials have been taken from the nonrelativistic ones. The coefficients A_{kl} have been determined by the MEFIT-optimization for $l = 0, 1, 2$ and by a SEFIT to the $5f^1\,{}^2F$ valence states for $l = 3$. The valence energies have been obtained from quasirelativistic all-electron HF calculations [14] by adding to the nonrelativistic Hartree–Fock operator a mass velocity term and a Darwin (averaged) spin–orbit term (in the form suggested by Wood and Boring [15] (WB)) cf. [1].

The method is similar to the quasirelativistic HF scheme of Cowan and Griffin [16] that has been used by other authors to derive one-component pseudopotentials which include the major relativistic effects (mass velocity and Darwin term, neglecting spin-orbit terms). Examples are the effective core potentials of Hay and Wadt [7, 8, 17] and the model potentials of Sakai et al. [9, 10]. Using these

approximate albeit well tested [18–20], quasirelativistic methods it is possible to calculate atomic all-electron reference energies and the corresponding pseudopotential valence energies within the *LS*-coupling scheme. This may be advantageous for the later use of the pseudopotentials in molecular calculations which are usually carried out in $\Lambda - S$-coupling. In contrast to this approach, Pacios and Christiansen [21], M. M. Hurley et al. [22], and LaJohn et al. [23] (following mainly the ideas in earlier work of Lee et al. [24], Ermler et al. [25] and Kahn et al. [26]) obtain shape consistent [27] averaged relativistic effective potentials from single-configuration average-energy Dirac-Fock wave functions, where the occupation numbers of the open shell orbitals are chosen to be close to but not necessarily equal to the exact averaging ratio of $l + 1$ to l. Our method differs from those of the other groups mentioned above in that our pseudopotentials are adjusted to total valence energies (corresponding to quantum mechanical observables) of a variety of states, instead of to orbitals or spinors and the corresponding orbital or spinor energies of a single state. Furthermore, our pseudopotentials are not constrained, by an a priori prescription, to a specific form in the chemically unimportant core region (which usually leads to a large number of terms in the analytical expansion of the pseudopotential and may cause instabilities in the nonlinear least-squares adjustment of the parameters [21]). Instead the parameters in the analytic expansion of our pseudopotentials are optimized directly in the fitting procedure, avoiding both the intermediate creation of a numerical pseudopotential and a subsequent analytic fit. Since no specific form of the pseudoorbitals is required in the core region we have the technical advantage that two Gaussian functions per angular quantum number l are usually sufficient to obtain an accurate pseudopotential. Furthermore our method is not restricted to the lowest nodeless pseudoorbitals within each symmetry. Therefore no difficulties due to the presence of several orbitals of the same symmetry [15, 21–23] are present, and excited atomic states are also applicable for the derivation of the pseudopotential.

The pseudopotentials derived in this work have been tested in atomic calculations for excitation and ionization energies [1]. The errors introduced by the pseudopotentials in comparison to all-electron results are always smaller than 0.05 eV in numerical HF calculations.

In order to apply our pseudopotentials in the molecular calculations presented in this paper $(7s6p5d)/[5s4p3d]$-GTO (Gaussian type orbital) valence basis sets have been energy optimized [28] in SCF calculations for the derived pseudopotentials of the rare earth elements Ln [1]. Errors in excitation and ionization energies due to the basis set expansion are smaller than 0.10 eV for all pseudopotentials. One or two additional f exponents have been energy optimized in CI(SD) calculations [29] and were applied in some calculations (LnX with Ln = La, Eu, Yb, Lu and X = H, O, F) to investigate basis set effects on molecular results.

For H we applied Huzinaga's $(5s)/[3s]$ GTO basis set [30] with one additional p function (exponent 1.2) to give a $(5s1p)/[3s1p]$ GTO basis set. For O and F Dunning's $(9s5p)/[4s2p]$ GTO basis set [31], together with his diffuse p function

[32], was used yielding a $(9s6p)/[4s3p]$ GTO basis set. For studying basis-set effects, Huzinaga's $(8s6p)/[3s3p]$ GTO basis set [30] for H was augmented by two diffuse s functions (exponents 0.02 and 0.01) and one d function (exponent 0.6) to give a $(10s6p1d)/[5s3p1d]$ GTO basis set, whereas for O and F one or two additional d functions [33] have been added.

3. Results

The results of our pseudopotential calculation will be discussed in terms of σ, π, δ valence subconfigurations and fixed atomic like $4f^n$ or $4f^{n+1}$ subconfigurations. As pointed out by Field [2], all electronic states arising from a $4f$ subconfiguration and the corresponding valence subconfiguration have nearly identical spectroscopic constants and may be considered to form a so-called superconfiguration. Since energetic splittings of states arising from the $4f$ subconfiguration in a molecular environment, as well as effects due to the different couplings within the $4f$ subconfiguration and to the valence subconfiguration, cannot be accounted for in our approach, we only calculate spectroscopic constants that are approximately valid for all states belonging to a superconfiguration. The discussion of experimental results is restricted to the lowest levels of the superconfigurations corresponding to divalent or trivalent rare earth metals. Following Field [2], superconfigurations will be characterized by an atomic $4f$ subconfiguration in parentheses and a molecular σ, π, δ valence subconfiguration. It is sufficient to specify only the highest occupied σ orbital for the superconfigurations considered in this work. In this section only pseudopotential results from CI(SD) calculations, which are corrected for size consistency by means of Davidson's formula [34], are discussed. A complete summary of bond lengths, dissociation energies, vibrational frequencies and dipole moments are given in Tables 1–8.

For all three series LnH, LnO and LnF (Ln = La − Lu) we found a nearly linear variation in the dissociation energies, calculated with respect to the reference configurations, as a function of the nuclear charge of the rare earth metal. By correcting the calculated values with the experimental energy separation of the atomic reference states, the experimentally observed characteristic nonmonotonic variation in the dissociation energies is reproduced, cf. Figs. 1 and 2 for LnO and LnF, respectively. This fact has been used by several authors to obtain approximate values of atomic excitation or ionization energies [35–38] or to discuss dissociation energies of rare earth monoxides in terms of a promotional model [39]. In the present work this feature is used to justify interpolation to other rare earth elements of results obtained in calculations performed for LnX with Ln = La, Eu, Yb, Lu and X = H, O, F using the quasirelativistic MEFIT, WB pseudopotentials and the largest basis sets.

The calculations have been performed with the program systems MELD/ATMOL [40] on a Cray-1 and MOLPRO [29] on a Cray-2. All spectroscopic constants have been derived from a third degree polynomial through 4 points of the potential curve with a spacing of 0.05 Å near the equilibrium distance. Dissociation energies

Table 1. Bond lengths of the rare earth monohydrides (Å) from SCF and CI(SD) calculations (including Davidson's correction ($+Q$)) and experiment. The core charges $Q = 11$ and $Q = 10$ denote the pseudopotentials for a $(4f^n)$ σ^2 and a $(4f^{n+1})$ σ^1 superconfiguration, respectively

LnH		$Q = 11$			$Q = 10$			Exp.	Ref.
		SCF	CI	$+Q$	SCF	CI	$+Q$		
LaH	a,d	2.094	2.066	2.075					
	b,d	2.098	2.082	2.089					
	c,d	2.094	2.077	2.084					
	b,e	2.095	2.079	2.085					
	c,e	2.076	2.057	2.062					
CeH	a,d	2.074	2.047	2.056					
PrH	a,d	2.057	2.032	2.042					
NdH	a,d	2.042	2.020	2.028	2.265	2.253	2.257		
PmH	a,d	2.031	2.011	2.020	2.254	2.242	2.247		
SmH	a,d	2.019	2.001	2.010	2.247	2.236	2.241		
EuH	a,d	2.007	1.990	1.999	2.240	2.230	2.235		
	b,d	2.020	2.010	2.017	2.235	2.225	2.232		
	b,e	2.014	1.997	2.002	2.225	2.199	2.203		
GdH	a,d	1.997	1.981	1.989					
TbH	a,d	1.990	1.978	1.986					
DyH	a,d	1.982	1.972	1.980					
HoH	a,d	1.976	1.967	1.975					
ErH	a,d	1.970	1.962	1.969					
TmH	a,d	1.965	1.958	1.965	2.182	2.164	2.169		
YbH	a,d	1.961	1.955	1.962	2.185	2.173	2.179	2.053	41
	b,d	1.982	1.976	1.981	2.159	2.148	2.156		
	b,e	1.975	1.958	1.963	2.146	2.126	2.132		
LuH	a,d	1.958	1.951	1.958				1.912	41
	b,d	1.975	1.968	1.973					
	b,e	1.968	1.949	1.954					

(a) MEFIT,HF pseudopotential
(b) MEFIT,WB pseudopotential
(c) As (b) but the f-pseudopotential is adjusted to La^{10+} $4f^1$ and $5f^1$ ^2F
(d) Ln $(7s6p5d)/[5s4p3d]$, H $(5s1p)/[3s1p]$
(e) Ln $(7s6p5d2f)/[5s4p3d2f]$, H $(10s5p1d)/[5s3p1d]$

were calculated with respect to the reference configurations of the neutral atoms and corrected by the experimental energy separations if necessary.

Monohydrides. Very little experimental data are available for the monohydrides of the rare earth elements. For the dissociation energy of YbH two upper bounds of 1.93 eV and 1.55 eV [41] are in good agreement with the value of 1.35 eV obtained in our best calculations using the quasirelativistic pseudopotential and the largest basis sets for the $(4f^{14})$ σ^1 superconfiguration. This pseudopotential result is ab initio since no correction with atomic excitation energies was necessary to calculate the dissociation energy with respect to the $(4f^{14})$ $6s^2$ reference configuration corresponding to the $4f^{14} 6s^2$ ^1S groundstate of Yb. In a similar calculation, the $(4f^{13})$ σ^2 superconfiguration is estimated to be 1.04 eV higher in energy, but this result had to be derived by correcting the dissociation energy of 3.91 eV, calculated with respect to the $(4f^{13})$ $5d^1 6s^2$ reference state, using the

Table 2. Bond lengths of the rare earth monoxides (Å) from SCF and CI(SD) calculations (including Davidson's correction (+Q)) and experiment. The core charges $Q = 11$ and $Q = 10$ denote the pseudopotentials for a $(4f^n)$ σ^1 and a $(4f^{n+1})$ σ^2 superconfiguration, respectively

LnO		$Q = 11$			$Q = 10$			Exp.	Ref.
		SCF	CI	+Q	SCF	CI	+Q		
LaO	a,d	1.945	1.983	1.999				1.826	41,52
	b,d	1.966	1.997	2.009					
	c,d	1.951	1.984	1.997					
	b,e	1.917	1.934	1.951					
	c,e	1.863	1.882	1.893					
	b,f	1.922	1.940	1.952					
	c,f	1.857	1.882	1.894					
CeO	a,d	1.924	1.960	1.974				1.820	41,(53)
PrO	a,d	1.913	1.949	1.964				1.801	41
								1.803	(54)
NdO	a,d	1.901	1.937	1.951					
PmO	a,d	1.889	1.923	1.938					
SmO	a,d	1.880	1.913	1.927	1.962	1.995	2.010		
EuO	a,d	1.870	1.903	1.917	1.957	1.990	2.004		
	b,d	1.873	1.906	1.920	1.963	1.998	2.015		
	b,e	1.840	1.852	1.863	1.933	1.942	1.954		
	b,f	1.844	1.856	1.867	1.934	1.943	1.955		
GdO	a,d	1.863	1.895	1.908				1.812	55
								1.809	(56)
TbO	a,d	1.853	1.884	1.897				1.814	(57)
DyO	a,d	1.847	1.876	1.889				1.796	(58, 59)
HoO	a,d	1.840	1.867	1.882				1.799	(59, 60)
ErO	a,d	1.834	1.862	1.875					
TmO	a,d	1.827	1.855	1.868	1.935	1.964	1.978		
YbO	a,d	1.823	1.851	1.863	1.931	1.962	1.978	1.807	(51)
	b,d	1.826	1.851	1.863	1.919	1.980	2.015		
	b,e	1.792	1.799	1.808	1.903	1.916	1.937		
	b,f	1.793	1.799	1.807	1.900	1.911	1.929		
LuO	a,d	1.819	1.846	1.858				1.790	41, 48
	b,d	1.818	1.842	1.852					
	b,e	1.788	1.793	1.801					
	b,f	1.786	1.791	1.800					

(a) MEFIT,HF pseudopotential
(b) MEFIT,WB pseudopotential
(c) As (b) but the f-pseudopotential is adjusted to La^{10+} $4f^1$ and $5f^1$ ^2F
(d) Ln $(7s6p5d)/[5s4p3d]$, O $(9s6p)/[4s3p]$
(e) Ln $(7s6p5d1f)/[5s4p3d1f]$, O $(9s6p1d)/[4s3p1d]$
(f) Ln $(7s6p5d2f)/[5s4p3d2f]$, O $(9s6p2d)/[4s3p2d]$
References given in parentheses indicate those experimental bond lengths that have been estimated from rotational constants

experimentally observed energy difference of 2.87 eV between the $4f^{14} 6s^2$ ^1S ground state and the $4f^{13} 5d^1 6s^2$ $(7/2, 3/2)_2$ excited state. An analogous procedure is applied throughout the paper to estimate the energy separations of super-configurations resulting from different f subconfigurations. The bond lengths and vibrational frequencies calculated for the $(4f^{14})$ σ^1 superconfiguration of YbH
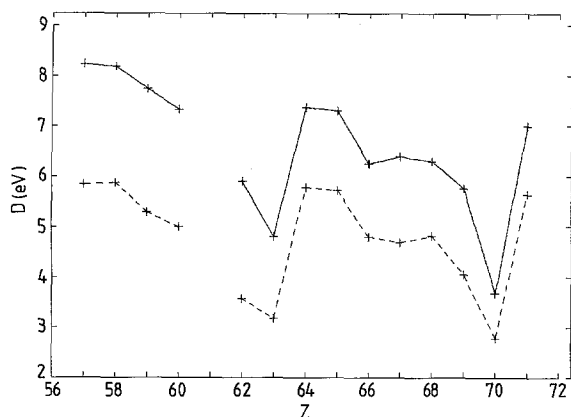
Fig. 1. Dissociation energies D_0 (eV) of the rare earth monooxides (Z denotes the nuclear charge of the rare earth metal) from nonrelativistic pseudopotential calculations (– – –) and experimental results (——)

($R_e = 2.13$ Å, $\omega_e = 1189$ cm^{-1}) are closer to the experimental values of the ground state ($R_e = 2.05$ Å, $\omega_e = 1250$ cm^{-1}) than those of the excited $(4f^{13})\ \sigma^2$ super-configuration ($R_e = 1.96$ Å, $\omega_e = 1443$ cm^{-1}). This is consistent with the above assignment which was made using dissociation energies. For the $(4f^{14})\ \sigma^2$ super-configuration of LuH the bond distance and vibrational frequency found in our best calculation ($R_e = 1.95$ Å, $\omega_e = 1445$ cm^{-1}) is also in reasonable agreement with the experimental values ($R_e = 1.91$ Å, $\omega_e = 1500$ cm^{-1}) of the ground state. Since we are not aware of an experimental value for the dissociation energy of LuH in literature, we compare our result of 3.24 eV, which is also ab initio, to the experimental value of 3.4 eV for LuD [41].

The errors introduced into the pseudopotential by the inclusion of the $4f$ orbitals in the core and the adjustment of the f pseudopotential to the ionization energies of the atomic $(4f^n$ or $4f^{n+1})\ 5f^1$ and $6f^1$ superconfigurations respectively may be estimated from an interpolation of the results for LaH and LuH. In the case of La the $4f$ orbitals are unoccupied in the ground state and the f part of the pseudopotential may, as usual, be adjusted to the $4f^1$ and $5f^1$ ^2F states of La^{10+}. The difference in the results obtained with this f potential and with the one
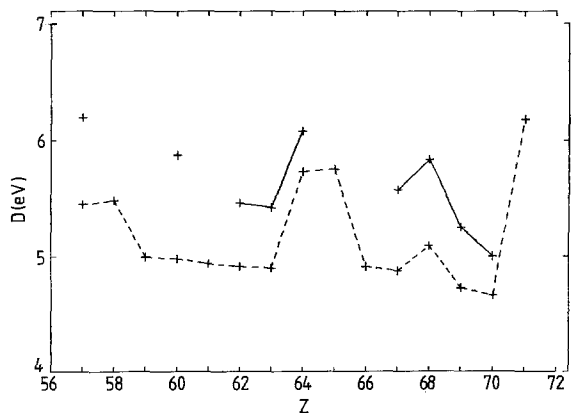

Fig. 2. Dissociation energies D_0 (eV) of the rare earth monofluorides (Z denotes the nuclear charge of the rare earth metal) from nonrelativistic pseudopotential calculations (– – –) and experimental results (——)

Table 3. Bond lengths of the rare earth monofluorides (Å) from SCF and CI(SD) calculations (including Davidson's correction ($+Q$)) and experiment. The core charges $Q = 11$ and $Q = 10$ denote the pseudopotentials for a $(4f^n)\ \sigma^2$ and a $(4f^{n+1})\ \sigma^1$ superconfiguration respectively

LnF		Q = 11			Q = 10			Exp.	Ref.
		SCF	CI	+Q	SCF	CI	+Q		
LaF	a,d	2.179	2.178	2.181				2.027	41
	b,d	2.173	2.179	2.183					
	c,d	2.161	2.169	2.172					
	b,e	2.123	2.115	2.116					
	c,e	2.081	2.070	2.072					
	b,f	2.124	2.116	2.118					
	c,f	2.080	2.068	2.070					
CeF	a,d	2.156	2.156	2.159					
PrF	a,d	2.142	2.142	2.145	2.240	2.249	2.252		
NdF	a,d	2.126	2.127	2.130	2.230	2.240	2.242		
PmF	a,d	2.110	2.112	2.115	2.216	2.226	2.229		
SmF	a,d	2.096	2.099	2.103	2.204	2.214	2.216		
EuF	a,d	2.083	2.087	2.090	2.193	2.203	2.206		
	b,d	2.074	2.084	2.088	2.190	2.204	2.208		
	b,e	2.028	2.020	2.022	2.155	2.144	2.145		
	b,f	2.026	2.017	2.018	2.151	2.138	2.138		
GdF	a,d	2.071	2.076	2.079					
TbF	a,d	2.059	2.065	2.067				1.960	61
DyF	a,d	2.048	2.055	2.059					
HoF	a,d	2.038	2.045	2.049				1.940	41
ErF	a,d	2.029	2.037	2.041					
TmF	a,d	2.020	2.029	2.033	2.136	2.146	2.148		
YbF	a,d	2.011	2.021	2.025	2.132	2.143	2.146	2.016	41
	b,d	1.999	2.013	2.017	2.119	2.136	2.140		
	b,e	1.959	1.953	1.955	2.085	2.079	2.080		
	b,f	1.953	1.944	1.946	2.078	2.066	2.067		
LuF	a,d	2.004	2.014	2.018				1.917	41
	b,d	1.989	2.002	2.007					
	b,e	1.950	1.944	1.946					
	b,f	1.944	1.934	1.936					

(a) MEFIT,HF pseudopotential
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(c) As (b) but the f-pseudopotential is adjusted to La^{10+} $4f^1$ and $5f^1$ ^2F
(d) Ln $(7s6p5d)/[5s4p3d]$, F $(9s6p)/[4s3p]$
(e) Ln $(7s6p5d1f)/[5s4p3d1f]$, F $(9s6p1d)/[4s3p1d]$
(f) Ln $(7s6p5d2f)/[5s4p3d2f]$, F $(9s6p2d)/[4s3p2d]$

adjusted to $5f^1$ and $6f^1$ ^2F (assuming that the $4f$ occupation number is zero) gives an indication of the magnitude of the errors in the molecular results at the beginning of the rare earth series. For LaH the (preferable) adjustment to the $4f^1$ and $5f^1$ ^2F states decreases the bond length by 0.03 Å and increases the dissociation energy by 0.47 eV, whereas the vibrational frequency remains almost unchanged. Since in the case of Lu the $4f$ orbitals are totally occupied and the adjustment to the $5f^1$ and $6f^1$ ^2F states is in any case not an approximation, we

Table 4. Dissociation energies of the rare earth monohydrides (eV) (AC denotes the CI(SD)+Q results after the energy correction to the experimentally observed atomic ground state of the rare earth atom was applied, cf. text)

LnH		Q = 11				Q = 10			Exp.	Ref.
		SCF	CI	+Q	+AC	SCF	CI	+Q		
LaH	a,d	1.72	2.35	2.42	2.42					
	b,d	1.89	2.50	2.57	2.57					
	c,d	1.90	2.51	2.58	2.58					
	b,e	2.00	2.61	2.71	2.71					
	c,e	2.06	3.02	3.18	3.18					
CeH	a,d	1.71	2.35	2.43	2.43					
PrH	a,d	1.71	2.36	2.43	1.88					
NdH	a,d	1.71	2.37	2.45	1.61	1.73	1.71	1.63		
PmH	a,d	1.73	2.39	2.46	—	1.69	1.67	1.59		
SmH	a,d	1.74	2.40	2.48	0.24	1.67	1.64	1.57		
EuH	a,d	1.75	2.42	2.50	−0.83	1.65	1.62	1.55		
	b,d	2.02	2.66	2.74	−0.59	1.30	1.28	1.23		
	b,e	2.14	2.72	2.82	−0.51	1.37	1.60	1.59		
GdH	a,d	1.77	2.44	2.52	2.52					
TbH	a,d	1.80	2.47	2.55	2.52					
DyH	a,d	1.83	2.50	2.59	1.65					
HoH	a,d	1.86	2.54	2.62	1.58					
ErH	a,d	1.90	2.58	2.66	1.77					
TmH	a,d	1.93	2.62	2.70	1.07	1.44	1.43	1.37		
YbH	a,d	1.98	2.67	2.74	−0.13	1.44	1.42	1.35	<1.93	41
	b,d	2.51	3.12	3.18	0.30	1.03	1.04	1.01		
	b,e	2.59	3.09	3.19	0.31	1.13	1.35	1.35		
LuH	a,d	2.02	2.71	2.79	2.79				(3.4	41, LuD)
	b,d	2.58	3.18	3.24	3.24					
	b,e	2.63	3.14	3.24	3.24					

(a)-(e) Cf. Table 1 for explanation

assume that errors due to our choice of the f potential are lower than the values obtained for LaH for all the rare earth monohydrides.

Taking into account these errors in the dissociation energies and making use of the linearity in the uncorrected dissociation energies, one finds (from interpolating the CI(SD)+Q results for the quasirelativistic MEFIT,WB pseudopotentials, together with the largest basis set, and correcting with the experimentally observed atomic energy separation of the reference states) that the ground states of LnH arise from a $(4f^n)$ σ^1 superconfiguration for Ln = La − Nd, Gd − Tm, Lu and from a $(4f^{n+1})$ σ^2 superconfiguration for Ln = Pm − Eu, Yb. Since no experimental data exist for molecules other than YbH and LuH these assignments are really predictions.

For LaH we also performed SCF calculations [42] with a two component pseudopotential (unpublished), where the correction term in the pseudopotential due to spin-orbit splitting were derived from all-electron DF (Dirac-Fock)

Table 5. Dissociation energies of the rare earth monoxides (eV) (AC denotes the CI(SD)+Q results after the energy correction to the experimentally observed atomic ground state of the rare earth atom was applied, cf. text)

LnO		Q = 11				Q = 10			Exp.	Ref.
		SCF	CI	+Q	+AC	SCF	CI	+Q		
LaO	a,d	3.54	5.49	5.84	5.84				8.23	41
	b,d	3.33	5.12	5.48	5.48				8.24	49
	c,d	3.45	5.22	5.57	5.57				>8.19	62
	b,e	4.02	5.75	6.28	6.28					
	c,e	4.59	6.22	6.74	6.74					
	b,f	4.15	5.85	6.42	6.42					
	c,f	4.75	6.33	6.89	6.89					
CeO	a,d	3.58	5.52	5.87	5.87				8.18	41
									8.22	49
PrO	a,d	3.54	5.48	5.84	5.29				7.74	41, 49
									7.63	63
NdO	a,d	3.53	5.47	5.83	4.99				7.33	41
									7.22	49, 63
PmO	a,d	3.54	5.47	5.83						
SmO	a,d	3.53	5.46	5.82	3.58	1.32	2.92	3.29	5.90	41
									5.77	49
EuO	a,d	3.52	5.43	5.79	2.46	1.21	2.81	3.18	4.80	41
	b,d	3.24	5.10	5.45	2.12	0.45	2.04	2.43	4.84	64
	b,e	3.88	5.59	6.13	2.79	0.76	2.46	3.02	4.85	65
	b,f	4.08	5.75	6.32	2.99	0.89	2.70	3.31	4.92	49
									4.97	66
GdO	a,d	3.50	5.42	5.78	5.78				7.37	41
									7.39	49
TbO	a,d	3.50	5.39	5.76	5.72				7.30	41
									7.33	49
DyO	a,d	3.49	5.37	5.73	4.80				6.25	41
HoO	a,d	3.49	5.37	5.72	4.68				6.39	41
									6.29	49
ErO	a,d	3.48	5.34	5.70	4.81				6.30	41
									6.31	49
									6.24	39
TmO	a,d	3.47	5.32	5.68	4.05	0.53	2.16	2.56	5.76	41
									5.16	49
YbO	a,d	3.47	5.31	5.66	2.79	0.41	2.01	2.40	<3.68 or	
	b,d	3.31	4.89	5.24	2.37	−0.35	1.31	1.78	>4.08	41
	b,e	3.80	5.35	5.87	2.99	−0.14	1.55	2.14	4.29	67
	b,f	3.96	5.54	6.10	3.22	0.00	1.82	2.45		
LuO	a,d	3.45	5.28	5.63	5.63				7.19	41
	b,d	3.36	4.93	5.28	5.28				6.99	49
	b,e	3.83	5.38	5.89	5.89					
	b,f	4.01	5.57	6.12	6.12					

(a)-(f) Cf. Table 2 for explanation

Table 6. Dissociation energies of the rare earth monofluorides (eV) (AC denotes the CI(SD)+Q results after the energy correction to the experimentally observed atomic ground state of the rare earth atom was applied, cf. text)

LnF		Q = 11				Q = 10			Exp.	Ref.
		SCF	CI	+Q	+AC	SCF	CI	+Q		
LaF	a,d	3.95	5.14	5.45	5.45				6.20	68
	b,d	4.35	5.46	5.77	5.77					
	c,d	4.40	5.50	5.81	5.81					
	b,e	4.70	5.55	5.98	5.98					
	c,e	4.90	5.68	6.11	6.11					
	b,f	4.79	5.56	6.02	6.02					
	c,f	4.98	5.68	6.15	6.15					
CeF	a,d	3.98	5.17	5.48	5.48					
PrF	a,d	3.99	5.19	5.50	4.95	4.37	4.84	4.99		
NdF	a,d	4.03	5.22	5.54	4.70	4.34	4.83	4.98	5.87	41
PmF	a,d	4.07	5.26	5.58		4.31	4.79	4.94		
SmF	a,d	4.11	5.31	5.63	3.39	4.29	4.77	4.91	5.46	41
									5.81	69
EuF	a,d	4.16	5.36	5.68	2.35	4.27	4.75	4.89	5.42	41
	b,d	4.66	5.77	6.09	2.76	3.89	4.38	4.51	5.60	69
	b,e	5.02	5.88	6.32	2.98	4.07	4.58	4.87		
	b,f	5.13	5.90	6.37	3.04	4.15	4.68	5.02		
GdF	a,d	4.21	5.41	5.73	5.73				6.08	41
TbF	a,d	4.27	5.46	5.78	5.75					
DyF	a,d	4.34	5.53	5.85	4.91				5.46	41
HoF	a,d	4.41	5.60	5.92	4.87				5.57	41
ErF	a,d	4.48	5.66	5.98	5.09				5.83	41
TmF	a,d	4.54	5.72	6.04	4.41	4.09	4.57	4.72	5.25	69
YbF	a,d	4.63	5.80	6.12	3.24	4.06	4.52	4.67	4.80	41
	b,d	5.35	6.38	6.69	3.81	3.59	4.03	4.20	5.00	70
	b,e	5.67	6.47	6.91	4.03	3.76	4.25	4.54		
	b,f	5.79	6.50	6.97	4.09	3.85	4.36	4.70		
LuF	a,d	4.70	5.87	6.18	6.18				(5.90, estimated 41)	
	b,d	5.43	6.45	6.76	6.76					
	b,e	5.75	6.56	6.99	6.99					
	b,f	5.85	6.57	7.04	7.04					

(a)–(f) Cf. Table 3 for explanation

calculations [43]. Virtually no changes in bond lengths or vibrational frequencies were obtained compared to the one component results. Since the program is only able to deal with closed shell systems, we did not derive a dissociation energy from the two component calculation.

Monoxides. The monoxides of the rare earth elements seem to be the most extensively experimentally investigated compounds studied in this work (cf. Tables 2, 6 and 7 for references). It was soon recognized that the nonmonotonic variation in the dissociation energies closely parallels the energies of the $4f^n$ to $4f^{n+1} 5d^1$ electronic transitions of the doubly ionized [44] or neutral [39] lanthanide atoms. This so-called promotional model [39] for the rare earth monoxides

assumes ground states belonging to a $(4f^n)$ σ^1 superconfiguration for all rare earth monoxides except for EuO and YbO, where ground states resulting from a $(4f^{n+1})$ σ^2 superconfiguration are proposed [2].

We find that the overall trend in the experimental dissociation energies is well reproduced in our calculations, cf. Fig. 1. Vibrational frequencies derived from our calculations are also in reasonable agreement with experimental values, however, the bond lengths calculated with our method are too large at the beginning of the series. E.g. for LaO we obtain values of 1.952 Å (f pseudo-potential adjusted to $5f$, $6f$) and 1.894 Å (f pseudopotential adjusted to $4f$, $5f$), respectively, in comparison with an experimental value of 1.826 Å [41]. In a corresponding calculation with the quasirelativistic effective core potential of Hay and Wadt [15] we obtained a bond length of 1.889 Å and a dissociation energy of 6.83 eV which is nearly identical with our best values of 1.894 Å and 6.89 eV respectively. The effect of core valence correlation was investigated by adding a core polarization potential to our pseudopotential, however all spectro-scopic constants remained virtually unchanged. (The analytic form of the polari-zation potential may be found in [45]; the dipole polarizability of the core was calculated [46] to be 0.4905 a.u.; the cut-off parameter δ of 1.0125 was adjusted to core-valence correlation energies of La^{10+} $5s^1$ ^2S calculated with CEPA-1 and an energy optimized $(16s12p10d3f)$ GTO (Gaussian Type Orbital) basis set.) Size consistency errors not accounted for by Davidson's correction [34] do not seem to be important since CEPA-1 (coupled electron pair approximation) [29, 47] calculations did not alter the CI(SD)+Q results. Finally, inclusion of a g potential into the pseudopotential, or addition of diffuse s, p, d functions on La and s, p functions on O only led to negligible changes in the results. We therefore feel that remaining errors in the bond length of LaO might be due to an insufficient treatment of electron correlation, i.e. that a MCSCF-MRCI (multi-configuration SCF-Multireference CI) would probably be necessary. The situation is considerably better at the end of the series: for the bond length of LuO, e.g., our value of 1.800 Å is close to the experimental value of 1.790 Å [41, 48].

Special attention was given to EuO and YbO where changes in the ground state superconfiguration are expected [2]. For EuO the thermochemically measured energy separation of 0.60 ± 0.13 eV [49] compares well with our result of 0.32 eV and the value of 0.41 eV obtained by Dulick et al. [49] from a ligand field model. The vibrational frequencies obtained in our calculations for the ground state superconfiguration (688 cm^{-1}) and the excited state superconfiguration (850 cm^{-1}) are in good agreement with the experimental values (668 cm^{-1}, 830 cm^{-1}) [49]. On the other hand, for YbO the thermochemical value of 0.05 ± 0.22 eV [49], the spectroscopic value of 0.11 eV [50] and the ligand field model results of 0.08 eV [49] are in contrast to our result, which places the $(4f^{14})$ σ^2 superconfiguration 0.77 eV higher in energy than the $(4f^{13})$ σ^1 superconfiguration. Unfortunately no vibrational frequencies have been measured for YbO. However, the rather small change in the equilibrium distance from YbO ($R_e = 1.807$ Å calculated from the rotational constant [51]) to LuO ($R_e = 1.790$ Å [41]) compares favourably to similar changes measured for LaO through PrO or GdO through HoO (cf. Table 2). It may be simply attributed to lanthanide contraction and not to a change in

Table 7. Vibrational frequencies ω_e (cm^{-1}) from CI(SD) calculations including Davidson's correction in comparison to experimental values (values for $\Delta G_{1/2}$ are given in parentheses)

Ln		LnH				LnO				LnF			
		$Q=11$	$Q=10$	Exp.	Ref.	$Q=11$	$Q=10$	Exp.	Ref.	$Q=11$	$Q=10$	Exp.	Ref.
La	a	1365				759		813	41	528		570	41
	b	1371				818				543			
	c	1450				829				571			
Ce	a	1375				753		828	71	532			
								820–825	72				
								808, 820	73				
								851	74				
								(824)	53				
Pr	a	1385				769		822	74	535	488		
								818	73				
								(830)	76				
Nd	a	1397	1133			768		815, 823	73	536	493		
Pm	a	1391	1131			775				540	496		
Sm	a	1406	1136			776	675	808, 819	73	542	498		
Eu	a	1410	1149			776	676	668	41	545	502		
	b	1386	1102			782	671	672	75	540	429		
	c	1474	1151			850	682			594	472		

Gd	a	1417			780		828	77	548		616	61
							813, 824	73				
							830	55				
							(824)	78				
Tb	a	1409			784		824	73, 41	542			
							828	75				
							(837)	57				
Dy	a	1415			776		829	73	544			
							(842)	58				
Ho	a	1426			784		829	73	545		615	41
							841	60				
Er	a	1422			785		829	73	545			
Tm	a	1423	1144		789	698	832	73	544	520		
Yb	a	1422	1167	1250 41	797	684	(683)	51	547	516	502	41
	b	1368	1153		749	568			533	437		
	c	1443	1189		849	624			599	478		
Lu	a	1427		1500 41	789		842	41	546		612	41
	b	1374			828		825, 811	73	532			
	c	1445			852		845	48	598			

(a) MEFIT,HF pseudopotential; Ln (7*s*6*p*5*d*)/[5*s*4*p*3*d*]; H (5*s*1*p*)/[3*s*1*p*]; O, F (9*s*6*p*)/[4*s*3*p*]
(b) MEFIT,WB pseudopotential; basis sets as indicated in (a)
(c) MEFIT,WB pseudopotential; Ln (7*s*6*p*5*d*2*f*)/[5*s*4*p*3*d*2*f*]; H (10*s*6*p*1*d*)/[5*s*3*p*1*d*]; O, F (9*s*6*p*2*d*)/[4*s*3*p*2*d*]

Table 8. Dipole moments (D) and derivatives with respect to the internuclear distance (D/Å) from CI(SD) calculations

Ln		LnH				LnO				LnF			
		Q = 11		Q = 10		Q = 11		Q = 10		Q = 11		Q = 10	
La	a	2.86	3.78			3.78	8.56			3.19	8.63		
	b	2.30	2.88			4.94	8.71			3.14	6.67		
	c	2.20	3.06			3.96	9.68			2.07	7.09		
Ce	a	2.78	3.68			3.80	8.09			3.13	8.44		
Pr	a	2.68	3.50			3.86	8.71			3.11	8.22	3.47	6.14
Nd	a	2.58	3.34	2.97	3.22	3.93	8.71			3.05	7.98	3.47	6.04
Pm	a	2.47	3.17	2.97	3.22	3.97	8.62			2.97	7.71	3.51	5.96
Sm	a	2.37	3.05	2.94	3.20	4.05	8.68	9.83	9.86	2.91	7.47	3.51	5.97
Eu	a	2.26	2.94	2.89	3.21	4.15	8.66	9.99	9.80	2.88	7.25	3.50	5.92
	b	1.90	2.66	3.22	3.25	5.41	8.58	10.30	9.01	2.99	5.89	4.22	5.80
	c	1.81	2.78	3.11	3.48	4.57	9.53	9.79	10.52	2.02	6.29	3.31	6.21
Gd	a	2.16	2.83			4.25	8.60			2.84	6.97		
Tb	a	2.06	2.72			4.34	8.48			2.78	6.75		
Dy	a	1.96	2.65			4.44	8.51			2.73	6.56		
Ho	a	1.87	2.59			4.52	8.54			2.69	6.36		
Er	a	1.79	2.56			4.65	8.46			2.67	6.22		
Tm	a	1.71	2.53	2.86	3.44	4.74	8.49	10.69	8.77	2.64	6.05	3.69	5.89
Yb	a	1.65	2.54	2.81	3.34	4.87	8.61	10.78	8.56	2.62	5.93	3.72	5.71
	b	1.70	3.08	3.02	3.47	6.04	8.27	10.63	8.18	2.99	5.44	4.42	5.72
	c	1.63	3.14	2.99	3.58	5.61	8.88	10.36	8.05	2.10	5.77	3.56	6.11
Lu	a	1.58	2.53			4.99	8.36			2.61	5.82		
	b	1.67	3.10			6.31	7.95			2.95	5.43		
	c	1.60	3.15			5.57	8.90			2.07	5.74		

(a)–(c) Cf. Table 7 for explanation

the superconfiguration. Therefore, in our view, a ground state belonging to a $(4f^{13})$ σ^1 superconfiguration seems to be possible for YbO.

Monofluorides. Most of the experimental information concerning the mono-fluorides of the rare earth elements is for dissociation energies, however some bond lengths and vibrational frequencies have been determined for LaF and the end of the series (cf. Tables 3, 4 and 7 for references). In contrast to the rare earth monoxides the characteristic double periodicity in the dissociation energies is not clearly apparent for the monofluorides. However, the trend in the dissoci-ation energies obtained from our calculations shows that the simple promotional model [39] developed for the monoxides will also be applicable to the mono-fluorides, cf. Fig. 2.

As already noted in the case of the monoxides the equilibrium distances obtained in our pseudopotential calculations are too large at the beginning and in reason-able agreement with experiment at the end of the rare earth series. The calculated values for the $(4f^0)$ σ^2 superconfiguration of LaF are 2.118 Å (f potential adjusted to $5f$ and $6f$) and 2.070 Å (f potential adjusted to $4f$ and $5f$) respectively and have to be compared with the experimental value of 2.027 Å [41]. For LuF our result of 1.936 Å is close to the experimental value of 1.917 Å [41]. The agreement of the calculated dissociation energies with experimental values is good in all cases, but we suggest that the estimated experimental value of 5.90 eV for LuF [41] may be considerably too low. Interpolating our results for the quasirelativistic pseudopotentials and the best basis sets from LaF, EuF, YbF and LuF to the other molecules we propose that the ground states of the rare earth monofluorides LnX belong to a $(4f^n)$ σ^2 superconfiguration for Ln = La – Nd, Gd – Tm and Lu or to a $(4f^{n+1})$ σ^1 superconfiguration for Ln = Pm – Eu and Yb. The change of the ground state at YbF does seem to be supported by corresponding experi-mentally observed nonmonotonic changes in the bond distances and vibrational frequencies in the second half of the rare earth series, however, for the first half of the series our assignments are predictions.

4. Conclusion

In the present paper it has been shown that reliable trends in spectroscopic constants for superconfigurations in series of compounds of rare earth elements may be obtained by application of pseudopotentials that include the partially filled $4f$ shell in the core. The work is the first systematic, albeit approximate, study on the rare earth monohydrides, monoxides and monofluorides and may be helpful for future experimental investigations of these compounds. In order to obtain quantitative results for specific states belonging to a superconfiguration, it will be necessary to include the $4f$ orbitals in the valence space, but problems are likely to arise in this case for the pseudopotential method with regard to the choice of the core and for both pseudopotential and all-electron approaches with regard to the treatment of electron correlation.

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