

## Energy-adjusted pseudopotentials for the rare earth elements

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Nonrelativistic and quasirelativistic energy-adjusted pseudopotentials and optimized  $(7s6p5d)/[5s4p3d]$ -GTO valence basis sets for use in molecular calculations for fixed  $f$ -subconfigurations of the rare earth elements, La through Lu, have been generated. Atomic excitation and ionization energies from numerical HF, as well as SCF pseudopotential calculations using the derived basis sets, differ by less than 0.1 eV from numerical HF all-electron results. Corresponding values obtained from CI(SD), CEPA-1, as well as density functional calculations using the quasirelativistic pseudopotentials, are in reasonable agreement with experimental data.

**Key words:** Pseudopotentials — Rare earth elements

### 1. Introduction

Pseudopotential methods [1-4] provide a reliable and convenient technique for quantum theoretical calculations on transition metal compounds [5, 6]. Due to the possibility of using a small optimized valence basis set, the computational effort is reduced considerably, at least at the SCF (self consistent field) level, in comparison to all-electron calculations. Moreover, relativistic effects [7] may be included in a simple way in SCF and subsequent CI (configuration interaction) calculations by adjusting the pseudopotentials to DF (Dirac Fock) or quasirelativistic data. Tables of accurate pseudopotentials for all transition metals and corresponding valence basis sets have been published recently by various authors [8-11].

For the rare earth elements we are not aware of any set of reliable pseudopotentials published in literature. Therefore, in this paper we present nonrelativistic and quasirelativistic energy-adjusted pseudopotentials, together with optimized valence basis sets, for the 4*f*-elements La through Lu.

In most ground or low-lying excited states of the transition metal atoms or ions the *nd*-orbitals ( $n = 3, 4, 5$ ) are partially occupied and errors in HF (Hartree Fock) energy levels obtained in all-electron frozen-core and pseudopotential calculations tend to depend on the *d*-occupation number, especially when the economically more preferable larger cores are used [5, 8–10]. The rare earth elements are even more complicated: due to the presence of the partially occupied 4*f*- and 5*d*-orbitals in most of the ground states or low-lying excited states, one might expect frozen-core, as well as pseudopotential errors, depending both on the *f*- and the *d*-occupancy. Moreover, as for transition metals (e.g. see [6, 12]), rather extensive correlation treatments and the inclusion of relativistic effects will be necessary to get results in reasonable agreement with experimental data, whether pseudopotential or all-electron calculations are performed.

From a chemical point of view rare earth elements are usually trivalent, less frequently bivalent (e.g. Eu and Yb) or tetravalent (e.g. Ce and Tb). This simple picture corresponds to the presence of atomic-like 4*f<sup>n</sup>* ( $n = 0-14$  for La–Lu), 4*f<sup>n+1</sup>* ( $n = 0-13$  for La–Yb) or 4*f<sup>n-1</sup>* ( $n = 1-14$  for Ce–Lu) subconfigurations in molecules.

Field [13] and coworkers developed a ligand field model to interpret the extremely complicated spectra of diatomic rare earth molecules. They also showed that, for the monoxides of the rare earth metals, all states belonging to a 4*f*-subconfiguration with a corresponding valence  $\sigma$ ,  $\pi$ ,  $\delta$ -subconfiguration have almost identical spectroscopic constants and might be considered to form a so-called super-configuration.

Orbital energies from all-electron HF calculations [14, 15] suggest that the 4*f*-orbitals belong to the valence space, however their spatial extent suggest they may be attributed to the core. This is supported by the fact that e.g. for Ce and Ce<sup>+</sup> the  $\langle r \rangle$ -expectation values of the 4*f*-orbitals in a *f*<sup>1</sup> or *f*<sup>2</sup> subconfiguration change by less than 1% for different valence *s*, *p*, *d*-configurations.

An almost negligible participation of the 4*f*-orbitals in chemical bonding of rare earth compounds has been found in an SCF study of the EuO<sub>6</sub><sup>2-</sup> cluster [16] as well as in INDO [17, 18] and  $X_\alpha$  studies [19, 20] of rare earth halogen compounds. Myers et al. [21] performed self-consistent charge EHMO calculations on rare earth metal trihalides and obtained reasonable results without explicitly including 4*f*-orbitals. Culberson et al. [18] point out that, at least in their INDO approach, some, albeit small, 4*f*-orbital contribution is necessary to obtain excellent agreement with experiment, especially for the bond lengths. Although the 4*f*-orbitals form an open shell they seem to have a core-like character, and the 5*d*- and 6*s*-valence orbitals (and their corresponding 6*s*<sup>2</sup>, 5*d*<sup>1</sup>6*s*<sup>2</sup> or 5*d*<sup>2</sup>6*s*<sup>2</sup> valence subconfigurations) are responsible for the observed chemical behaviour of the lanthanides.

In light of these results we attribute the  $4f$ -orbitals to the core and attempt to adjust our pseudopotentials for a fixed  $4f$ -subconfiguration. In this way we avoid pseudopotential errors depending on the  $f$ -occupation number. Differential relativistic and correlation effects resulting from changes in the valence  $s$ ,  $p$ ,  $d$ - or  $\sigma$ ,  $\pi$ ,  $\delta$ -subconfigurations are treated by adjusting our pseudopotentials to quasirelativistic all-electron data and performing a valence CI(SD), CEPA or density functional calculation respectively. As for the  $3d$ -transition metals, where an inclusion of the  $3s$ - and  $3p$ -orbitals in the valence space usually improves the quality of the pseudopotentials [5, 8–11], we consider the  $5s$ - and  $5p$ -orbitals of the rare earth elements as valence orbitals. By means of this and our method of adjusting the pseudopotentials to several valence substates we reduce pseudopotential errors depending on the  $d$ -occupation number. Moreover, we suggest that energy differences between states of different  $f$ -occupancies derived e.g. from CI calculations using our quasirelativistic pseudopotentials should be corrected with the experimentally observed energy separation [22] between the lowest LSJ-levels of the  $4f^n 5d^1 6s^2$  and  $4f^{n+1} 6s^2$ -configurations respectively. Thus, although only approximately, a large portion of differential relativistic and correlation effects due to changes in the  $f$ -orbital occupancy is also accounted for.

In this paper we present pseudopotentials for the  $4f^n$  and the  $4f^{n+1}$  subconfigurations from which e.g. all ground states of the lanthanide atoms and ions [22]  $\text{Ln}^{n+}$  ( $n=0-3$ ) and the rare earth monoxides may be derived [13]. Density functional, CI(SD), and CEPA results of atomic excitation and ionization energies from calculations with the generated pseudopotentials are compared to experimental values. In a forthcoming paper corresponding results from already completed molecular calculations for  $\text{LnH}$ ,  $\text{LnO}$ ,  $\text{LnF}$ ,  $\text{Ln}_2$  and  $\text{LnX}_3$  ( $\text{Ln} = \text{La-Lu}$ ,  $\text{X} = \text{F, Cl, Br, J}$ ) will be reported.

## 2. Method

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

$$H = -\frac{1}{2} \sum_i \Delta_i + \sum_i V(r_i) + \sum_{i < j} \frac{1}{r_{ij}}$$

where  $V(r_i)$  is a semilocal pseudopotential of the form

$$V(r_i) = -\frac{Q}{r_i} + \sum_i \sum_k A_{kl} \exp(-a_{kl} r_i^2) P_l.$$

$Q$  denotes the charge of the core,  $i$  and  $j$  are electron indices and  $P_l$  is the projection operator onto the Hilbert subspace with angular symmetry  $l$

$$P_l = \sum_{m_l} |lm_l\rangle \langle lm_l|.$$

### 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 obtained separately, for each value of the quantum number  $l$ , in a single

electron fit (SEFIT [23]) to the HF-valence energies [14] of the  $\text{Ln}^{(Q-1)+} 1s^2 \dots 4f^m nl^1 {}^2L$  valence substates of the 'one-valence electron' ions ( $n = 5-8$ ;  $l = s, p, d, f$ ;  $L = S, P, D, F$ ; 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). Since our pseudopotentials are designed to yield results valid for all electronic states belonging to a single superconfiguration arising from a specific  $4f$ -subconfiguration for the  $4f$  orbitals, only an average coupling [15] was taken into account. Moreover, terms for angular quantum number  $l = 4$  were not included in the pseudopotentials, because their effect on molecular results turned out to be negligible.

In a second step the coefficients  $A_{kl}$  ( $l = 0, 1, 2$ ) have been improved in a multi electron fit (MEFIT [24]) by adjusting them in a least-squares fit to the HF-valence energies [14] of 8 (divalent) or 10 (trivalent) low-lying valence substates of Ln and  $\text{Ln}^+$ . The  $f$ -pseudopotential was not modified in this step, and by means of its adjustment to the valence energies of the  $5f^1$  and  $6f^2 F$  valence substates it 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 as in the second step described above ( $l = 0, 1, 2$ ) and by a SEFIT to the  $5f^1 {}^2F$  valence states ( $l = 3$ ), respectively. The valence energies have, however, been obtained from quasirelativistic all-electron HF calculations [24]. A mass-velocity term

$$h_{mv,i} = -\left(\frac{\alpha^2}{2}\right)(V_i(r) - \varepsilon_i)^2$$

and an (averaged) Darwin-spin-orbit term

$$h_{Dso,i} = -\left(\frac{\alpha^2}{4}\right)\frac{dV_i}{dr}B_i\left(\frac{d}{dr} - \frac{1}{r}\right)$$

with

$$B_i = \left[1 + \left(\frac{\alpha^2}{2}\right)(\varepsilon_i - V_i(r))\right]^{-1}$$

in the form suggested by Wood and Boring [25] (WB), where  $\alpha \cong 1/137.036$  is the fine-structure constant, are added to the nonrelativistic Hartree-Fock operator  $F_{nrel,i}$  for the  $i$ th orbital  $\phi_i$ :

$$[F_{nrel,i} + h_{mv,i} + h_{Dso,i}]\phi_i = \varepsilon_i\phi_i.$$

Due to the nonlocal exchange operators in the HF equations [15] it is not possible

to define a well-behaved local potential function  $V_i(r)$  to be used in the quasi-relativistic operators. We therefore approximate  $V_i(r)$  in the mass-velocity and Darwin-spin-orbit term by

$$V_i(r) = -\frac{Z}{r} + V_{C,i}(r) + V_{X,i}(r)$$

where  $Z$  is the charge of the nucleus,  $V_{C,i}(r)$  is the HF Coulomb potential (without self-interaction) and  $V_{X,i}(r)$  denotes Slater's local potential approximation for the HF exchange potential [26] (multiplied by a scaling parameter  $\alpha = 2/3$ ) corrected for self interaction according to Perdew and Zunger [27]. For calculating the total energy in our quasirelativistic calculations we simply add the expectation values of the quasirelativistic operators to the one-electron matrix elements of the nonrelativistic energy expression. The method outlined above is similar to the HFR method of Cowan and Griffin [28]: for excitation and ionization energies of the transition metals e.g. we obtain agreement with the HFR results of Martin and Hay [29] within 0.1 eV. A comparison of our WB results with DF data is given in Table 1 for La and Lu. A deeper discussion of the problems associated with quasirelativistic methods was given by Karwowski and Kobus [30] and in the original papers [25, 28].

The parameters of the derived MEFIT-pseudopotentials are listed in Table 2.

( $7s6p5d$ )/[ $5s4p3d$ ]-GTO (Gaussian type orbital) valence basis sets for use in subsequent molecular calculations have been energy optimized [31] for the  $5d^1 6s^1 6p^1$  valence subconfiguration of the  $4f^n$  subconfiguration and for the  $6s^2$  ( $s$ -basis),  $6s^1 6p^1$  ( $p$ -basis) and  $5d^1 6s^1$  ( $d$ -basis) valence subconfigurations of the  $4f^{n+1}$  subconfiguration in calculations using the nonrelativistic MEFIT pseudopotentials. For the quasirelativistic MEFIT pseudopotentials the exponents were left unchanged, however the contraction coefficients were optimized for the configurations mentioned above. All basis sets are summarized in Table 3.

**Table 1.** Comparison of excitation and ionization energies (eV) of La and Lu from (averaged) DF [41], quasirelativistic WB [24] and HF [14] all-electron calculations

State			DF	WB	HF		DF	WB	HF		
$5d^1$	$6s^2$	$^2D$	La	0.00	0.00	0.00	Lu	0.00	0.00	0.00	
	$6s^2$	$6p^1$	$^2P$	La	1.81	1.84	2.55	Lu	0.29	0.32	1.46
	$6s^2$		$^1S$	La <sup>+</sup>	5.59	5.61	6.40	Lu <sup>+</sup>	4.34	4.36	5.63
$5d^1$			$^2D$	La <sup>++</sup>	14.75	14.74	14.10	Lu <sup>++</sup>	17.90	17.88	16.35
	$6s^1$		$^2S$	La <sup>++</sup>	16.15	16.16	16.61	Lu <sup>++</sup>	16.95	16.96	17.43
		$6p^1$	$^2P$	La <sup>++</sup>	19.66	19.68	19.69	Lu <sup>++</sup>	21.87	21.90	21.39
$4f^1$			$^2F$	La <sup>++</sup>	16.70	16.62	13.48				

**Table 2.** Parameters (in atomic units) of the nonrelativistic (HF) and quasirelativistic (WB) MEFIT-pseudopotentials corresponding to  $4f^{n+1}$  ( $Q=10.$ ) and  $4f^n$  ( $Q=11.$ ) subconfigurations in La through Lu

Ln	$l$	$k$	$Q=10$			$Q=11$			
			$A_{kl}$	HF	$A_{kl}$ WB	$a_{kl}$	$A_{kl}$	HF	$A_{kl}$ WB
La	0	1	90.755796		90.163456	3.3862	97.442563	91.932177	3.3099
	0	2	-0.133089		-3.430454	1.6931	-1.543210	-3.788764	1.6550
	1	1	62.630852		62.516467	2.8552	65.110902	63.759486	2.8368
	1	2	0.114875		-0.840750	1.4276	0.005873	-0.647958	1.4184
	2	1	28.783323		28.794835	1.9523	37.262863	36.116173	2.0213
	2	2	0.381812		0.412229	0.9762	-0.161458	0.219114	1.0107
	3	1	8.720231		10.882080	0.9818	8.176586	8.592705	0.9366
Ce	0	1	100.210580		99.528143	3.6400	95.537821	95.842155	3.5222
	0	2	-0.875999		-4.328411	1.8200	-0.108883	-3.775040	1.7611
	1	1	68.380251		68.246478	3.0673	68.312710	68.092779	3.0177
	1	2	0.001628		-1.134774	1.5337	0.035977	-0.966756	1.5089
	2	1	30.457733		30.460371	2.0876	36.352201	36.381848	2.1443
	2	2	0.147021		0.108142	1.0438	0.028939	0.190447	1.0722
	3	1	7.001895		7.624485	0.8839	10.456021	12.704802	1.1623
Pr	0	1	111.076955		110.308394	3.9099	102.978663	102.244372	3.7437
	0	2	-0.876095		-5.374318	1.9550	-0.340283	-4.298146	1.8719
	1	1	43.460490		43.427586	2.6955	72.025284	71.807871	3.2066
	1	2	-0.224519		-1.080556	1.3478	0.123928	-1.070291	1.6033
	2	1	32.324713		32.296212	2.2301	37.386492	37.407043	2.2720
	2	2	-0.133099		-0.264880	1.1151	-0.038832	0.059971	1.1366
	3	1	6.896105		7.420821	0.9146	8.581705	9.256679	1.0575
Nd	0	1	123.467469		122.314966	4.1964	111.148378	110.314639	3.9755
	0	2	-0.738113		-6.178775	2.0982	-0.496858	-5.078210	1.9878
	1	1	82.163876		79.852477	3.5308	76.141493	75.868939	3.4045
	1	2	-0.296461		-1.545026	1.7654	0.178552	-1.172553	1.7023
	2	1	34.354685		37.226658	2.3797	38.263506	38.271906	2.4044
	2	2	-0.177220		-0.898127	1.1899	-0.043904	-0.026339	1.2022
	3	1	6.851461		7.331006	0.9514	8.477735	9.062814	1.0917
Pm	0	1	137.680814		136.702998	4.5022	118.304826	117.358370	4.2184
	0	2	-1.105724		-7.321072	2.2511	-0.266255	-5.509273	2.1092
	1	1	90.596336		90.371852	3.7871	81.256174	80.979260	3.6118
	1	2	-0.384256		-2.330083	1.8936	0.095829	-1.450760	1.8059
	2	1	36.612340		36.578156	2.5392	39.133955	39.096573	2.5435
	2	2	-0.377953		-0.689124	1.2696	-0.022928	-0.067584	1.2718
	3	1	6.819062		7.266695	0.9899	8.440270	8.983167	1.1321
Sm	0	1	154.407988		153.167043	4.8312	126.847664	125.808087	4.4735
	0	2	-1.232706		-8.592215	2.4156	-0.188875	-6.169188	2.2368
	1	1	100.276801		98.845412	4.0613	86.647189	86.294826	3.8294
	1	2	-0.576684		-2.655907	2.0307	0.068422	-1.686917	1.9147
	2	1	39.212940		41.022141	2.7083	40.159013	40.149862	2.6882
	2	2	-0.574857		-1.292004	1.3542	-0.018044	-0.140083	1.3441
	3	1	6.793012		7.217476	1.0297	8.410018	8.925543	1.1741

Table 2 (continued)

Ln	<i>l</i>	<i>k</i>	<i>Q</i> = 10			<i>Q</i> = 11			
			<i>A<sub>kl</sub></i>	HF	<i>A<sub>kl</sub></i> WB	<i>a<sub>kl</sub></i>	<i>A<sub>kl</sub></i>	HF	<i>A<sub>kl</sub></i> WB
Eu	0	1	174.081377		172.797896	5.1852	138.554829	125.972804	4.7421
	0	2	-1.226048		-10.092260	2.5926	-0.581743	-5.265472	2.3711
	1	1	111.585056		111.315027	4.3588	91.907886	86.395920	4.0592
	1	2	-0.816194		-3.402558	2.1794	0.208076	-1.042461	2.0286
	2	1	41.938963		41.867729	2.8902	41.595486	40.156495	2.8407
	2	2	-0.715378		-1.287433	1.4451	-0.058114	-0.099115	1.4204
	3	1	6.770040		7.176158	1.0705	8.389432	8.885019	1.2176
Gd	0	1	198.333463		196.814708	5.5709	152.721910	139.601619	5.0260
	0	2	-1.793250		-11.909078	2.7855	-1.143406	-6.879694	2.5130
	1	1	125.378770		123.936252	4.6807	97.478201	79.873824	4.3022
	1	2	-0.962356		-3.969076	2.3404	0.400624	0.938419	2.1511
	2	1	45.228107		47.132939	3.0851	43.189475	32.709729	3.0011
	2	2	-0.988173		-1.958724	1.5426	-0.106225	1.241952	1.5055
	3	1	6.745511		7.136831	1.1120	8.370213	8.849776	1.2620
Tb	0	1	227.722670		226.166240	5.9916	162.865255	139.661156	5.3260
	0	2	-2.135565		-14.100361	2.9958	-0.754823	-5.767915	2.6630
	1	1	142.066193		141.695166	5.0346	105.515736	79.049864	4.5598
	1	2	-1.206586		-4.965426	2.5173	0.267958	1.864568	2.2799
	2	1	49.063785		48.981700	3.2977	44.481981	35.140886	3.1707
	2	2	-1.243710		-2.067529	1.6489	-0.069222	0.879040	1.5854
	3	1	6.722666		7.103860	1.1546	8.350673	8.818477	1.3073
Dy	0	1	264.776093		262.980927	6.4567	180.769020	139.869617	5.6450
	0	2	-2.590344		-16.758471	3.2284	-1.353241	-4.609163	2.8225
	1	1	162.676390		162.035711	5.4243	112.610791	79.192669	4.8337
	1	2	-1.484095		-5.965211	2.7122	0.471004	2.716029	2.4169
	2	1	53.604558		53.897843	3.5298	46.517961	35.156964	3.3506
	2	2	-1.543307		-2.614492	1.7649	-0.124442	0.961701	1.6753
	3	1	6.701321		7.073257	1.1981	8.330264	8.788667	1.3534
Ho	0	1	312.597297		310.596178	6.9754	197.602711	140.021658	5.9851
	0	2	-3.015997		-20.099095	3.4877	-1.388663	-3.321543	2.9925
	1	1	188.906122		188.411299	5.8588	121.587585	78.571698	5.1262
	1	2	-1.871333		-7.275582	2.9294	0.517126	3.792278	2.5631
	2	1	59.091175		58.955765	3.7844	51.364449	37.419462	3.5417
	2	2	-1.895275		-3.142476	1.8922	-0.586780	0.655290	1.7708
	3	1	6.682591		7.050293	1.2430	8.313825	8.766488	1.4008
Er	0	1	376.479559		374.239829	7.5616	216.820671	140.180496	6.3499
	0	2	-3.788509		-24.396164	3.7808	-1.536544	-1.892132	3.1750
	1	1	223.370065		222.801107	6.3499	132.260177	77.420855	5.4402
	1	2	-2.280203		-8.921413	3.1750	0.578452	5.075405	2.7201
	2	1	65.756340		65.615556	4.0682	54.472404	41.554697	3.7467
	2	2	-2.323734		-3.849665	2.0341	-0.746224	0.040595	1.8733
	3	1	6.665317		7.031122	1.2891	8.016275	8.447022	1.4266

Table 2 (continued)

Ln	<i>l</i>	<i>k</i>	<i>Q</i> = 10			<i>Q</i> = 11					
			<i>A<sub>kl</sub></i>	HF	<i>A<sub>kl</sub></i> WB	<i>a<sub>kl</sub></i>	<i>A<sub>kl</sub></i>	HF	<i>A<sub>kl</sub></i> WB	<i>a<sub>kl</sub></i>	
Tm	0	1	465.447015		462.865094	8.2347	239.141472		140.826395		6.7422
	0	2	-4.640558		-30.107435	4.1174	-2.290637		-0.486662		3.8711
	1	1	270.572636		269.892838	6.9143	144.745814		78.871092		5.7795
	1	2	-2.874946		-11.102004	3.4572	0.620242		6.026297		2.8897
	2	1	74.404111		72.257562	4.3874	58.022213		38.219360		3.9658
	2	2	-2.874287		-4.485908	2.1937	-0.928731		0.743298		1.9829
	3	1	6.652959		7.020401	1.3369	8.280626		8.730362		1.4988
Yb	0	1	595.254325		592.068534	9.0224	271.538565		140.926118		7.1674
	0	2	-5.675700		-37.940480	4.5112	-2.443382		1.454935		3.5837
	1	1	337.500494		334.845493	7.5724	159.285860		76.745228		6.1460
	1	2	-3.679612		-13.865410	3.7862	0.715586		7.766207		3.0730
	2	1	85.148886		90.539904	4.7503	62.083331		46.067636		4.2030
	2	2	-3.471327		-6.634958	2.3752	-1.102109		-0.482389		2.1015
	3	1	6.643897		7.016510	1.3864	8.270963		8.722119		1.5500
Lu	0	1					299.806838		141.300211		7.6315
	0	2					-2.015183		3.493950		3.8157
	1	1					177.414461		76.059248		6.5463
	1	2					0.695491		9.440662		3.2731
	2	1					59.213397		49.091473		4.4597
	2	2					-0.184093		-0.846410		2.2298
	3	1					8.264490		8.722955		1.6030

### 3. Results

Differential relativistic effects in excitation and ionization energies derived from our HF and WB all-electron calculations, see Tables 4–6, supplement the values given by Martin and Hay [29] for the  $5d$ -transition metals. Relativistic effects for a fixed  $4f^n$  or  $4f^{n+1}$  subconfiguration tend to stabilize the states with small  $d$ -occupation number and are in general below 3.0 eV, cf. Tables 5 and 6. However, differential relativistic effects in the energy separation between the  $4f^n 5d^1 6s^2$  and  $4f^{n+1} 6s^2$  configurations increase from 2.6 eV for La to up to 4.7 eV for Yb and stabilize the states with the lower  $f$ -occupation number, cf. Table 6. Differential correlation effects, estimated from the difference of the WB and experimental values, tend to stabilize the states with the higher  $f$ -occupation number and are relatively small for the first half of the row but become as large as the differential relativistic effects in the second half of the row when electron pairing occurs in the  $f$ -shell.

Results for atomic excitation and ionization energies obtained by numerical HF and SCF pseudopotential calculations using the derived basis sets are presented in Tables 5 and 6. The maximum deviations from the all-electron reference valence



**Table 3.** Contraction coefficients and exponents of the  $(7s6p5d)/[5s4p3d]$ -GTO valence basis sets

Ln	Q = 10			Q = 11			
	Coefficients		Exponents	Coefficients		Exponents	
	MEFIT, HF	MEFIT, WB		MEFIT, HF	MEFIT, WB		
La	s	-0.098516	-0.032853	6.395111	-0.695806	-0.417243	5.087399
		1.071088	0.839278	3.345488	1.271164	0.886010	4.270978
		-1.916352	-1.753724	2.076428	-1.521992	-1.419752	1.915458
		1.	1.	0.422369	1.	1.	0.525596
		1.	1.	0.207463	1.	1.	0.263474
	p	1.	1.	0.045303	1.	1.	0.048820
		1.	1.	0.019470	1.	1.	0.022836
		0.575294	0.503820	3.077176	0.612175	0.538196	3.025161
		-1.163627	-1.048061	2.298746	-1.088467	-0.981640	2.382095
		1.303812	1.285971	0.593457	1.255347	1.239590	0.584426
	d	1.	1.	0.282592	1.	1.	0.260360
		1.	1.	0.119706	1.	1.	0.083334
		1.	1.	0.030222	1.	1.	0.030275
		-0.183315	-0.184161	1.364358	-0.099993	-0.096944	1.576824
		0.330194	0.325192	0.813882	0.427935	0.407466	0.592390
Ce	s	0.841979	0.846203	0.327788	0.687462	0.704363	0.249500
		1.	1.	0.122378	1.	1.	0.106513
		1.	1.	0.040677	1.	1.	0.045831
		-0.152097	-0.056554	6.404325	-0.881939	-0.523004	5.320774
		0.914702	0.670452	3.853784	1.387275	0.935594	4.670955
	p	-1.706492	-1.561795	2.126538	-1.453871	-1.364722	1.975943
		1.	1.	0.446310	1.	1.	0.536180
		1.	1.	0.218416	1.	1.	0.266026
		1.	1.	0.046475	1.	1.	0.050225
		1.	1.	0.020040	1.	1.	0.023391
	d	0.718186	0.625430	3.145009	0.472034	0.416129	3.315982
		-1.262067	-1.127987	2.492037	-0.928796	-0.842652	2.494951
		1.278031	1.260593	0.610160	1.241120	1.226841	0.606150
		1.	1.	0.283074	1.	1.	0.268989
		1.	1.	0.113904	1.	1.	0.084431
Pr	s	1.	1.	0.030402	1.	1.	0.030721
		-0.169243	-0.170139	1.471779	-0.090251	-0.090270	1.714204
		0.326329	0.324195	0.848867	0.413569	0.395699	0.633410
		0.835300	0.837365	0.340950	0.696217	0.711933	0.265842
		1.	1.	0.126329	1.	1.	0.110889
	p	1.	1.	0.041647	1.	1.	0.045204
		-0.147085	-0.052601	6.982832	-0.704670	-0.381171	5.761840
		0.830775	0.598180	4.204143	1.176213	0.757064	4.958606
		-1.627519	-1.493758	2.211163	-1.420359	-1.328780	2.045497
		1.	1.	0.464103	1.	1.	0.550185
	d	1.	1.	0.226820	1.	1.	0.269269
		1.	1.	0.047940	1.	1.	0.051433
		1.	1.	0.020585	1.	1.	0.023552

Table 3 (continued)

Ln	Q = 10			Q = 11				
	Coefficients		Exponents	Coefficients		Exponents		
	MEFIT, HF	MEFIT, WB		MEFIT, HF	MEFIT, WB			
<i>p</i>	0.232569	0.196174	3.595261	0.324753	0.281039	3.657448		
	-0.675082	-0.600452	2.336053	-0.747960	-0.674402	2.567810		
	1.249188	1.229743	0.632452	1.220343	1.206107	0.618410		
	1.	1.	0.282392	1.	1.	0.270256		
	1.	1.	0.104371	1.	1.	0.086632		
	1.	1.	0.030195	1.	1.	0.031224		
	<i>d</i>	-0.148748	-0.148374	1.580354	-0.072092	-0.072146	1.985686	
		0.323086	0.321535	0.865833	0.423829	0.407652	0.631268	
		0.825385	0.826418	0.342348	0.671852	0.686470	0.271432	
		1.	1.	0.125047	1.	1.	0.114545	
1.		1.	0.042319	1.	1.	0.046139		
Nd	<i>s</i>	-0.171437	-0.056273	7.232655	-0.544845	-0.274141	6.375654	
		0.819527	0.558797	4.531657	0.973374	0.609793	5.333679	
		-1.591242	-1.450655	2.292665	-1.377695	-1.289341	2.106318	
		1.	1.	0.482189	1.	1.	0.562955	
		1.	1.	0.235717	1.	1.	0.271797	
	<i>p</i>	1.	1.	0.048071	1.	1.	0.052549	
		1.	1.	0.020649	1.	1.	0.023724	
		0.783397	0.650938	3.539388	0.228137	0.194497	4.078140	
		-1.311119	-1.125628	2.844179	-0.623210	-0.560942	2.644687	
		1.259850	1.238330	0.662186	1.202491	1.188835	0.631374	
<i>d</i>	1.	1.	0.305571	1.	1.	0.271939		
	1.	1.	0.122996	1.	1.	0.086577		
	1.	1.	0.031627	1.	1.	0.031366		
	-0.087168	-0.094192	1.920386	-0.065129	-0.065017	2.167628		
	0.349292	0.351213	0.737339	0.425564	0.412433	0.652584		
	0.745650	0.746613	0.328522	0.666291	0.678187	0.280851		
	1.	1.	0.126990	1.	1.	0.118467		
	1.	1.	0.042946	1.	1.	0.047360		
	Pm	<i>s</i>	-0.186268	-0.069638	7.809123	-0.438978	-0.206019	6.655687
			0.759684	0.515529	5.015979	0.968280	0.616182	5.251255
-1.516532			-1.394264	2.365243	-1.475780	-1.361497	2.308910	
1.			1.	0.508509	1.	1.	0.577283	
1.			1.	0.246696	1.	1.	0.286338	
<i>p</i>		1.	1.	0.049279	1.	1.	0.054295	
		1.	1.	0.021136	1.	1.	0.025226	
		0.488232	0.405592	3.926539	0.321271	0.270562	4.095185	
		-1.009440	-0.876796	2.875247	-0.800453	-0.709106	2.782455	
		1.256891	1.236558	0.689530	1.250091	1.231526	0.701567	
<i>d</i>	1.	1.	0.309723	1.	1.	0.307882		
	1.	1.	0.119435	1.	1.	0.098951		
	1.	1.	0.031793	1.	1.	0.033772		
	-0.077178	-0.076654	2.102186	-0.066836	-0.066632	2.315014		
	0.359373	0.363397	0.746000	0.392074	0.382790	0.717612		
	0.731202	0.727484	0.329619	0.693697	0.701977	0.318968		

Table 3 (continued)

Ln	Q = 10				Q = 11			
	Coefficients		Exponents	Coefficients		Exponents		
	MEFIT, HF	MEFIT, WB		MEFIT, HF	MEFIT, WB			
	<i>d</i>	1.	1.	0.126902	1.	1.	0.130435	
		1.	1.	0.042738	1.	1.	0.049851	
Sm	<i>s</i>	-0.640086	-0.288766	7.084211	-1.150544	-0.563323	6.477588	
		1.184521	0.698986	5.842530	1.676450	0.961496	5.791813	
		-1.486640	-1.353122	2.463103	-1.471967	-1.349481	2.412584	
		1.	1.	0.537541	1.	1.	0.606601	
		1.	1.	0.259698	1.	1.	0.300832	
		1.	1.	0.049710	1.	1.	0.055202	
		1.	1.	0.021408	1.	1.	0.025731	
	<i>p</i>	0.306475	0.246822	4.377422	0.483938	0.405992	4.026092	
		-0.818225	-0.707500	2.869505	-0.941083	-0.822491	3.045263	
		1.255084	1.233425	0.716078	1.234173	1.215545	0.720567	
		1.	1.	0.311385	1.	1.	0.313021	
		1.	1.	0.111548	1.	1.	0.097310	
		1.	1.	0.031707	1.	1.	0.033798	
		<i>d</i>	-0.069710	-0.072513	2.292144	-0.076865	-0.076284	2.176192
0.366938	0.373134		0.757583	0.393144	0.385532	0.778621		
0.720894	0.716343		0.331443	0.709222	0.715687	0.323910		
1.	1.		0.126638	1.	1.	0.131924		
1.	1.		0.042383	1.	1.	0.051322		
Eu	<i>s</i>		-0.678120	-0.288775	7.497197	-0.514693	-0.189307	7.363006
			1.246033	0.708008	6.172556	1.010519	0.541995	5.973380
		-1.508161	-1.365699	2.608166	-1.441756	-1.305800	2.492572	
		1.	1.	0.530389	1.	1.	0.621781	
		1.	1.	0.254033	1.	1.	0.305007	
		1.	1.	0.052202	1.	1.	0.057444	
		1.	1.	0.022110	1.	1.	0.026696	
	<i>p</i>	1.337307	1.108217	3.994342	0.204905	0.155289	4.844781	
		-1.803769	-1.525182	3.503617	-0.628352	-0.528887	2.980927	
		1.218030	1.198663	0.722399	1.215533	1.192228	0.730440	
		1.	1.	0.324354	1.	1.	0.310774	
		1.	1.	0.127842	1.	1.	0.096286	
		1.	1.	0.033028	1.	1.	0.033753	
		<i>d</i>	-0.111799	-0.127297	2.061708	-0.061590	-0.058297	2.534693
0.320218	0.377785		0.967971	0.385352	0.381498	0.784388		
0.805496	0.765795		0.369101	0.704330	0.706725	0.332098		
1.	1.		0.128958	1.	1.	0.130759		
1.	1.		0.041927	1.	1.	0.049390		
Gd	<i>s</i>		-0.211783	-0.065984	8.988100	-0.447331	-0.152264	7.925043
			0.914911	0.594025	5.659589	0.933901	0.493923	6.271759
		-1.640816	-1.471996	2.837122	-1.431873	-1.294553	2.590913	
		1.	1.	0.536949	1.	1.	0.642509	
		1.	1.	0.258361	1.	1.	0.312826	
		1.	1.	0.053156	1.	1.	0.058480	
		1.	1.	0.023090	1.	1.	0.026924	

Table 3 (continued)

Ln	Q = 10			Q = 11			
	Coefficients		Exponents	Coefficients		Exponents	
	MEFIT, HF	MEFIT, WB		MEFIT, HF	MEFIT, WB		
<i>p</i>	1.503775	1.175174	4.226905	0.178159	0.114143	5.205055	
	-2.169326	-1.739817	3.598566	-0.576638	-0.442610	3.111021	
	1.297180	1.268417	0.821919	1.199301	1.166532	0.743765	
	1.	1.	0.404963	1.	1.	0.312702	
	1.	1.	0.180465	1.	1.	0.094375	
<i>d</i>	1.	1.	0.035489	1.	1.	0.033614	
	-0.104472	-0.108424	2.255244	-0.060504	-0.039487	2.534209	
	0.312145	0.325698	1.004982	0.394926	0.390831	0.806732	
	0.803642	0.794308	0.393628	0.704932	0.701628	0.320355	
	1.	1.	0.136938	1.	1.	0.124207	
	1.	0.043213	1.	1.	0.048091		
Tb	<i>s</i>	-0.332729	-0.117334	9.012892	-0.896370	-0.269035	7.744790
		0.974528	0.590718	6.353074	1.414084	0.607153	6.718832
		-1.578585	-1.416772	2.928434	-1.461757	-1.291295	2.744470
		1.	1.	0.547085	1.	1.	0.655116
		1.	1.	0.252626	1.	1.	0.322594
<i>p</i>	1.	1.	0.054520	1.	1.	0.059871	
	1.	1.	0.022438	1.	1.	0.027830	
	3.610444	2.678714	4.302434	0.353787	0.209138	4.853856	
	-4.510532	-3.396760	3.898279	-0.809791	-0.562461	3.407141	
	1.330450	1.316390	0.897458	1.227624	1.180541	0.806550	
	1.	0.493517	1.	1.	0.346971		
	1.	0.218933	1.	1.	0.110326		
	1.	0.036875	1.	1.	0.036443		
<i>d</i>	-0.097105	-0.096999	2.411351	-0.073706	-0.052831	2.517057	
	0.312406	0.327859	1.027819	0.362846	0.362090	0.921149	
	0.800315	0.787880	0.396178	0.739053	0.732119	0.371697	
	1.	1.	0.135462	1.	1.	0.142102	
	1.	1.	0.042594	1.	1.	0.052675	
Dy	<i>s</i>	-0.515636	-0.457000	8.679818	-0.841359	-0.183085	8.166604
		0.815630	0.893540	7.440385	1.373331	0.503621	6.996564
		-0.770670	-1.379065	3.036265	-1.474724	-1.274668	2.875581
		1.	1.	0.564126	1.	1.	0.670155
		1.	1.	0.263460	1.	1.	0.329607
<i>p</i>	1.	1.	0.056100	1.	1.	0.061275	
	1.	1.	0.023338	1.	1.	0.028373	
	0.543696	2.608815	4.586385	0.352110	0.190367	5.075819	
	-0.735832	-3.603007	4.004981	-0.794206	-0.519525	3.579856	
	0.213289	1.413372	1.050262	1.217537	1.165940	0.828312	
	1.	0.526827	1.	1.	0.354331		
	1.	0.221300	1.	1.	0.111802		
	1.	0.037400	1.	1.	0.036922		
<i>d</i>	-0.036834	-0.092460	2.565152	-0.068095	-0.044536	2.686207	
	0.125759	0.332345	1.054322	0.364890	0.366137	0.941717	
	0.318597	0.783155	0.398949	0.735324	0.725974	0.376196	
	1.	1.	0.134440	1.	1.	0.142362	
	1.	1.	0.041885	1.	1.	0.052561	

Table 3 (continued)

Ln	Q = 10			Q = 11			
	Coefficients		Exponents	Coefficients		Exponents	
	MEFIT, HF	MEFIT, WB		MEFIT, HF	MEFIT, WB		
Ho	<i>s</i>	-0.634974	-0.262489	9.485824	-0.784894	-0.054278	8.604622
		1.271725	0.727639	7.494493	1.313669	0.206702	7.302424
		-1.570192	-1.405889	3.211659	-1.470929	-0.650361	2.986714
		1.	1.	0.571299	1.	1.	0.692968
		1.	1.	0.264451	1.	1.	0.340107
		1.	1.	0.057569	1.	1.	0.062381
	<i>p</i>	1.829900	1.319149	4.800736	0.374215	0.091472	5.244049
		-2.770629	-2.063116	4.000046	-0.800674	-0.242999	3.779376
		1.354534	1.337527	0.989254	1.206649	0.575601	0.848159
		1.	1.	0.530936	1.	1.	0.359935
		1.	1.	0.235388	1.	1.	0.111614
		1.	1.	0.037947	1.	1.	0.037175
	<i>d</i>	-0.094021	-0.093763	2.669896	-0.070237	-0.023517	2.807694
		0.316060	0.336628	1.104716	0.364602	0.197492	0.975974
		0.799544	0.783105	0.408636	0.736870	0.387117	0.387382
		1.	1.	0.135635	1.	1.	0.145901
		1.	1.	0.041710	1.	1.	0.053564
		Er	<i>s</i>	-1.001404	-0.441839	9.584261	-1.055446
1.630251	0.900028			8.110572	1.580872	0.362977	7.791355
-1.561124	-1.398022			3.333734	-1.466858	-1.224290	3.108828
1.	1.			0.600814	1.	1.	0.716583
1.	1.			0.279532	1.	1.	0.351534
1.	1.			0.057862	1.	1.	0.064005
<i>p</i>	2.715067		1.979780	5.158700	0.474700	0.210649	5.318881
	-3.873273		-2.897887	4.373876	-0.886020	-0.486538	4.058153
	1.324894		1.380486	1.108107	1.195063	1.134001	0.866503
	1.		1.	0.562051	1.	1.	0.366404
	1.		1.	0.236888	1.	1.	0.113294
	1.		1.	0.038473	1.	1.	0.037662
<i>d</i>	-0.080772		-0.080218	2.985953	-0.066780	-0.044421	2.980840
	0.316512		0.339920	1.098370	0.364816	0.372796	1.002725
	0.788655		0.769472	0.412903	0.735952	0.721617	0.393945
	1.		1.	0.136036	1.	1.	0.146754
	1.		1.	0.041379	1.	1.	0.053573
	Tm		<i>s</i>	-1.226035	-0.571502	10.110929	-0.431728
1.831219		1.015179		8.769498	0.964252	0.201271	7.757389
-1.536217		-1.382616		3.446655	-1.472818	-1.200363	3.244999
1.		1.		0.618476	1.	1.	0.685675
1.		1.		0.285610	1.	1.	0.328837
1.		1.		0.055954	1.	1.	0.067800
<i>p</i>		1.	1.	0.023490	1.	1.	0.030553
		0.538457	0.423048	6.843761	0.295875	0.112293	5.930103
		-2.319722	-2.014458	3.513773	-0.694850	-0.371216	4.069733

Table 3 (continued)

Ln	Q = 10			Q = 11		
	Coefficients		Exponents	Coefficients		Exponents
	MEFIT, HF	MEFIT, WB		MEFIT, HF	MEFIT, WB	
<i>p</i>	1.706480	1.849824	1.499491	1.187954	1.124752	0.886356
	1.	1.	0.558104	1.	1.	0.368834
	1.	1.	0.218687	1.	1.	0.111505
	1.	1.	0.038781	1.	1.	0.037591
	-0.079538	-0.076821	3.072349	-0.068356	-0.035480	3.124778
	0.325690	0.349957	1.119160	0.360143	0.370334	1.055430
	0.785893	0.765503	0.402318	0.739910	0.720006	0.416732
<i>d</i>	1.	1.	0.129700	1.	1.	0.155912
	1.	1.	0.039491	1.	1.	0.056348
	-0.347255	-0.131653	11.624442	-0.910062	0.031538	9.938236
	1.346778	0.877344	7.429509	1.431945	0.188469	8.542512
	-1.924017	-1.678091	3.979089	-1.461428	-1.179628	3.355371
	1.	1.	0.592689	1.	1.	0.759043
	1.	1.	0.280461	1.	1.	0.370337
<i>s</i>	1.	1.	0.058380	1.	1.	0.068041
	1.	1.	0.023827	1.	1.	0.031509
	1.531274	1.193125	5.706376	0.219693	0.067082	6.498028
	-1.982926	-1.580640	5.021693	-0.595824	-0.297409	4.151066
	1.188417	1.167384	0.913209	1.174816	1.109221	0.896693
	1.	1.	0.392740	1.	1.	0.365319
	1.	1.	0.148453	1.	1.	0.108505
<i>p</i>	1.	1.	0.036586	1.	1.	0.037193
	-0.070733	-0.735074	3.439423	-0.056750	-0.034327	3.475614
	0.310094	0.339878	1.142757	0.387888	0.403715	1.016376
	0.791115	0.767804	0.417754	0.710000	0.689281	0.397858
	1.	1.	0.127548	1.	1.	0.154461
	1.	1.	0.038334	1.	1.	0.057101
	Lu	<i>s</i>			-0.521401	-0.106096
				1.023270	0.420378	8.741727
				-1.441271	-1.264278	3.454870
				1.	1.	0.778870
				1.	1.	0.377476
<i>p</i>				1.	1.	0.069468
				1.	1.	0.032013
				0.253465	0.083923	6.631599
				-0.618097	-0.311474	4.424413
				1.165624	1.105117	0.915253
<i>d</i>				1.	1.	0.370843
				1.	1.	0.109044
				1.	1.	0.037502
				-0.049891	-0.049611	3.665216
				0.366270	0.377217	1.076071
		0.730986	0.721475	0.408988		
		1.	1.	0.147706		
		1.	1.	0.053093		

energies is smaller than 0.05 eV for all presented pseudopotentials and all reference states at the numerical HF level. The maximum error in excitation and ionization energies in comparison to all-electron results is also less than 0.05 eV. The maximum error in excitation and ionization energies introduced by the basis set expansion is lower than 0.1 eV for all cases.

We performed additional CI(SD) calculations [32], allowing for excitations from all orbitals, and estimating the contribution of quadruple excitations by means of Davidson's correction [33]. We also applied self-interaction corrected [34] and gradient corrected [35, 36] density functionals, which have been discussed in detail in previous papers [37, 38]. Densities from numerical HF calculations [24] were used to calculate correlation contributions to excitation and ionization energies. It seems to be difficult to judge the quality of our results summarized in Tables 5 and 6: on the one hand we are not aware of any all-electron CI calculations for rare-earth elements, and on the other hand the experimental data [22] are too incomplete to perform a proper averaging over  $J$ -levels and different couplings of the  $f$ -electrons. Moreover, due to the strong mixing of different configurations with equal  $J$ , the averaging would in any case be questionable. We therefore compare our results for excitation and ionization energies to experimental values determined by using only the lowest  $LSJ$ -levels of each configuration [22]. Due to this approximation only a rough agreement may be expected. In general, the density functional results are closer to the experimental values than the CI results.

As it is shown in Tables 7 and 8 for La, Yb and Lu, the CI results improve slightly upon adding a single  $f$ -function, optimized to give the lowest CI(SD) energy for the  $5d^16s^2$  valence subconfiguration of La ( $4f^0$  subconfiguration;

**Table 4.**  $4f^n$  ( $^xX$ )  $5d^16s^2$   $^yY \rightarrow 4f^{n+1}6s^2$   $^zZ$  energy separation (eV) from HF [14] and WB [25] all-electron calculations; vector coupling coefficients were calculated with the program LSTERMS [42]; results for the average energy of the configuration are given in parentheses; experimental values [22] refer to the energy separation between the lowest levels of each configuration, respectively

	$n$	$^xX$	$^yY$	$^zZ$	HF	WB	Exp.
La	0		$^2D$	$^2F$	0.08 (0.08)	2.71 (2.71)	1.88
Ce	1	$^2F$	$^1G$	$^3H$	-1.28 (-0.78)	1.55 (1.95)	0.59
Pr	2	$^3H$	$^4I$	$^4I$	-2.91 (-1.52)	0.02 (1.32)	-0.55
Nd	3	$^4I$	$^5L$	$^5I$	-2.92 (-2.15)	0.21 (0.81)	-0.84
Pm	4	$^5I$	$^6L$	$^6H$	-2.76 (-2.71)	0.48 (0.39)	
Sm	5	$^6H$	$^7F$	$^7F$	-4.48 (-3.20)	-1.09 (0.05)	-2.27
Eu	6	$^7F$	$^8D$	$^8S$	-6.01 (-3.63)	-2.35 (-0.23)	-3.45
Gd	7	$^8S$	$^9D$	$^7F$	1.19 (-4.01)	4.64 (-0.45)	1.36
Tb	8	$^7F$	$^8G$	$^6H$	-0.46 (-4.34)	3.19 (-0.61)	-0.04
Dy	9	$^6H$	$^7H$	$^5I$	-1.97 (-4.63)	1.88 (-0.72)	-0.94
Ho	10	$^5I$	$^6I$	$^4I$	-1.81 (-4.88)	2.18 (-0.79)	-1.04
Er	11	$^4I$	$^5G$	$^3H$	-1.80 (-5.10)	2.35 (-0.82)	-0.89
Tm	12	$^3H$	$^4K$	$^2F$	-3.09 (-5.27)	1.29 (-0.80)	-1.63
Yb	13	$^2F$	$^3H$	$^1S$	-5.09 (-5.42)	-0.44 (-0.75)	-2.88

**Table 5.** Excitation and ionization energies (eV) from numerical HF [14] and WB [24] all-electron (AE) calculations compared to results obtained with the non-relativistic MEFIT, HF and the quasirelativistic MEFIT, WB pseudopotentials from numerical HF [24] and SCF [31] calculations using the optimized ( $7s6p5d$ )/[ $5s4p3d$ ]-GTO basis sets. CI(SD) [32] results corrected for size consistency errors + Q[33] and density functional results ([25]; SPP [34], GCP [35]; GCL [36]) compared to experimental data [22]. All data refer to a  $f^{n+1}$  subconfiguration and a  $s^2$  S valence substate of the rare earth elements La–Yb  $n = 0-13$

Ln	AE HF	MEFIT, HF HF	AE WB	MEFIT, WB HF	MEFIT, WB SCF	MEFIT, HF CI(SD) + Q	SPP	GCP	GCL	MEFIT, WB CI(SD) + Q	SPP	GCP	GCL	Exp.
Ln $5d^1 6s^1 3D$ valence substate:														
La	0.37	0.37	0.37	0.92	0.92	1.06	1.22	0.66	0.43	1.58	1.73	1.03	1.05	1.02
Ce	0.45	0.44	0.44	1.02	1.02	1.12	1.30	0.73	0.50	1.69	1.84	1.14	1.16	0.91
Pr	0.54	0.54	0.55	1.13	1.14	1.24	1.40	0.84	0.61	1.81	1.96	1.26	1.29	1.00
Nd	0.64	0.64	0.64	1.25	1.26	1.33	1.49	0.95	0.71	1.93	2.07	1.40	1.43	1.05
Pm	0.74	0.75	0.75	1.38	1.39	1.44	1.60	1.06	0.83	2.06	2.20	1.76	1.54	1.05
Sm	0.85	0.86	0.86	1.52	1.52	1.55	1.71	1.18	0.94	2.19	2.34	1.91	1.69	1.34
Eu	0.97	0.97	0.98	1.66	1.68	1.65	1.81	1.30	1.07	2.33	2.47	2.06	1.84	1.60
Gd	1.08	1.08	1.09	1.79	1.80	1.74	1.90	1.42	1.19	2.44	2.58	2.21	2.00	1.65
Tb	1.20	1.20	1.21	1.93	1.94	1.84	2.00	1.55	1.32	2.56	2.69	2.37	2.15	1.87
Dy	1.32	1.32	1.32	2.07	2.08	1.95	2.11	1.68	1.45	2.69	2.83	2.52	2.31	2.17
Ho	1.43	1.44	1.44	2.21	2.22	2.06	2.21	1.81	1.58	2.83	2.96	2.67	2.47	2.34
Er	1.55	1.55	1.55	2.35	2.36	2.18	2.33	1.94	1.72	2.96	3.09	2.83	2.63	2.40
Tm	1.67	1.67	1.67	2.48	2.49	2.29	2.44	2.07	1.85	3.09	3.22	2.98	2.79	2.53
Yb	1.79	1.79	1.79	2.62	2.62	2.43	2.59	2.20	1.98	3.25	3.38	3.13	2.94	3.04
Ln $5d^2 3F$ valence substate:														
La	1.58	1.57	1.58	2.54	2.53	2.54	2.73	1.70	1.40	3.50	3.67	2.74	2.47	2.42
Ce	1.74	1.72	1.74	2.73	2.74	2.70	2.89	1.85	1.55	3.72	3.89	2.96	2.69	2.72
Pr	1.92	1.93	1.95	2.96	2.97	3.00	3.10	2.07	1.77	3.95	4.13	3.19	2.94	2.94
Nd	2.12	2.12	2.14	3.20	3.21	3.24	3.09	2.27	1.98	4.19	4.36	3.45	3.20	2.71
Pm	2.32	2.33	2.35	3.46	3.46	3.50	3.30	2.49	2.21	4.44	4.61	3.72	3.48	3.49
Sm	2.53	2.53	2.56	3.72	3.72	3.76	3.50	2.71	2.43	4.70	4.87	4.00	3.76	3.78
Eu	2.75	2.74	2.81	3.98	3.99	4.08	3.69	2.94	2.67	4.96	5.13	4.28	4.05	3.95
Gd	2.96	2.96	2.99	4.24	4.25	4.28	3.88	3.17	2.91	5.20	5.36	4.57	4.35	4.38
Tb	3.18	3.18	3.21	4.51	4.52	4.55	4.28	3.41	3.15	5.44	5.59	4.86	4.64	4.68
Dy	3.40	3.40	3.43	4.78	4.79	4.81	4.45	3.64	3.39	5.70	5.84	5.15	4.94	4.98
Ho	3.62	3.61	3.65	5.05	5.06	5.07	4.49	3.88	3.63	5.96	6.10	5.44	5.24	5.28
Er	3.84	3.83	3.87	5.32	5.33	5.34	4.70	4.11	3.87	6.22	6.37	5.73	5.53	5.58
Tm	4.05	4.05	4.07	5.59	5.60	5.59	4.91	4.35	4.11	6.48	6.63	6.02	5.83	5.89
Yb	4.27	4.27	4.29	5.86	5.87	5.85	5.15	4.58	4.36	6.78	6.92	6.30	6.13	6.19



Ln<sup>+</sup> 6s<sup>1</sup> 2S valence substate:

La	4.20	4.19	4.19	4.37	4.35	4.35	4.76	4.92	4.80	4.99	5.41	4.93	5.08	4.96	5.15	5.58	5.45
Ce	4.26	4.25	4.25	4.44	4.42	4.42	4.82	4.98	4.86	5.05	5.47	5.00	5.16	5.04	5.23	5.66	5.43
Pr	4.31	4.31	4.30	4.50	4.49	4.48	4.89	5.05	4.92	5.11	5.53	5.08	5.23	5.11	5.30	5.73	5.46
Nd	4.36	4.34	4.34	4.56	4.54	4.54	4.92	5.08	4.96	5.15	5.57	5.14	5.29	5.17	5.36	5.80	5.53
Pm	4.41	4.39	4.39	4.63	4.60	4.60	4.98	5.14	5.02	5.21	5.63	5.20	5.35	5.23	5.43	5.86	5.55
Sm	4.45	4.44	4.44	4.69	4.66	4.66	5.02	5.19	5.06	5.25	5.68	5.26	5.41	5.30	5.49	5.93	5.64
Eu	4.50	4.47	4.47	4.74	4.72	4.71	5.06	5.23	5.10	5.29	5.72	5.32	5.47	5.36	5.55	5.99	5.67
Gd	4.54	4.52	4.52	4.80	4.78	4.77	5.09	5.25	5.16	5.34	5.77	5.36	5.51	5.42	5.61	6.05	
Tb	4.58	4.56	4.56	4.86	4.83	4.83	5.12	5.28	5.20	5.39	5.82	5.40	5.55	5.48	5.67	6.12	5.86
Dy	4.62	4.61	4.60	4.92	4.89	4.89	5.17	5.32	5.25	5.43	5.87	5.46	5.60	5.54	5.73	6.18	5.94
Ho	4.67	4.64	4.64	4.97	4.95	4.94	5.20	5.36	5.29	5.47	5.91	5.52	5.66	5.60	5.79	6.24	6.02
Er	4.71	4.69	4.68	5.03	5.00	5.00	5.25	5.40	5.34	5.52	5.96	5.57	5.71	5.66	5.85	6.30	6.11
Tm	4.75	4.73	4.72	5.09	5.06	5.05	5.30	5.46	5.38	5.56	6.00	5.64	5.78	5.72	5.91	6.36	6.18
Yb	4.79	4.76	4.76	5.15	5.12	5.11	5.37	5.53	5.42	5.60	6.04	5.73	5.88	5.78	5.96	6.43	6.25

Ln<sup>+</sup> 5d<sup>1</sup> 2D valence substate:

La	4.37	4.37	4.37	5.22	5.19	5.19	5.40	5.61	4.69	4.76	5.12	6.23	6.43	5.56	5.65	6.03	5.75
Ce	4.50	4.49	4.49	5.39	5.37	5.37	5.53	5.74	4.81	4.88	5.24	6.42	6.62	5.75	5.84	6.22	5.82
Pr	4.65	4.65	4.66	5.58	5.56	5.56	5.70	5.92	4.98	5.05	5.42	6.62	6.82	5.94	6.03	6.42	5.95
Nd	4.80	4.79	4.79	5.78	5.76	5.76	5.83	6.04	5.13	5.19	5.56	6.82	7.01	6.15	6.24	6.63	6.07
Pm	4.96	4.96	4.96	5.99	5.97	5.97	6.01	6.22	5.30	5.37	5.73	7.03	7.22	6.37	6.46	6.85	6.21
Sm	5.13	5.12	5.12	6.21	6.19	6.19	6.17	6.37	5.46	5.53	5.89	7.25	7.44	6.59	6.69	7.08	6.53
Eu	5.30	5.28	5.28	6.43	6.41	6.41	6.31	6.51	5.63	5.70	6.06	7.47	7.66	6.82	6.92	7.31	6.90
Gd	5.47	5.46	5.46	6.66	6.64	6.63	6.47	6.67	5.82	5.89	6.25	7.66	7.85	7.06	7.16	7.55	
Tb	5.65	5.63	5.63	6.89	6.87	6.85	6.62	6.82	6.00	6.07	6.44	7.87	8.05	7.30	7.40	7.80	7.26
Dy	5.83	5.81	5.81	7.12	7.10	7.08	6.79	6.99	6.18	6.26	6.63	8.10	8.28	7.54	7.65	8.05	7.78
Ho	6.01	5.99	5.99	7.36	7.34	7.31	6.96	7.16	6.37	6.44	6.81	8.32	8.50	7.79	7.90	8.30	8.04
Er	6.19	6.18	6.18	7.60	7.58	7.55	7.14	7.34	6.56	6.64	7.01	8.56	8.74	8.04	8.16	8.56	8.16
Tm	6.38	6.36	6.35	7.84	7.82	7.77	7.33	7.52	6.75	6.83	7.20	8.81	8.99	8.30	8.41	8.82	8.37
Yb	6.56	6.54	6.55	8.09	8.07	8.01	7.56	7.76	6.95	7.03	7.40	9.09	9.33	8.55	8.67	9.08	9.10

**Table 6.** As Table 5, but for the  $f^n$  subconfiguration and with respect to a  $5d^1 6s^2 D$  valence substate of the rare earth elements La-Lu ( $n = 0-14$ )

Ln	AE HF	MEFIT, HF	HF SCF	AE WB	MEFIT, WB	SCF	MEFIT, HF CI(SD) +Q	SPP	GCP	GCL	MEFIT, WB CI(SD) +Q	SPP	GCP	GCL	Exp.
<b>Ln <math>5d^2 6s^1 4f</math> valence substate:</b>															
La	-0.98	-1.01	-1.00	-0.30	-0.33	-0.32	-0.10	0.13	-0.57	-0.89	-0.84	-0.57	-0.89	-0.84	0.33
Ce	-0.92	-0.90	-0.93	-0.22	-0.24	-0.23	-0.04	0.20	-0.50	-0.82	-0.77	-0.50	-0.82	-0.77	0.29
Pr	-0.84	-0.86	-0.85	-0.11	-0.13	-0.12	0.04	0.27	-0.41	-0.74	-0.69	-0.41	-0.74	-0.69	0.28
Nd	-0.76	-0.77	-0.76	0.00	-0.01	-0.01	0.13	0.36	-0.32	-0.64	-0.59	-0.32	-0.64	-0.59	0.27
Pm	-0.66	-0.68	-0.67	0.13	0.11	0.12	0.22	0.44	-0.22	-0.55	-0.49	-0.22	-0.55	-0.49	0.20
Sm	-0.56	-0.58	-0.57	0.26	0.25	0.26	0.31	0.54	-0.11	-0.44	-0.38	-0.11	-0.44	-0.38	0.56
Eu	-0.46	-0.47	-0.46	0.39	0.39	0.40	0.42	0.64	0.01	-0.32	-0.26	0.01	-0.32	-0.26	0.42
Gd	-0.35	-0.31	-0.35	0.54	0.55	0.55	0.53	0.76	0.13	-0.20	-0.14	0.13	-0.20	-0.14	0.79
Tb	-0.24	-0.25	-0.24	0.69	0.69	0.70	0.63	0.86	0.25	-0.08	-0.02	0.25	-0.08	-0.02	0.98
Dy	-0.12	-0.13	-0.12	0.84	0.85	0.85	0.76	0.97	0.38	0.05	0.11	0.38	0.05	0.11	1.35
Ho	0.00	-0.01	0.00	0.99	1.01	1.01	0.86	1.09	0.51	0.18	0.25	0.51	0.18	0.25	1.46
Er	0.12	0.11	0.12	1.15	1.16	1.17	0.98	1.20	0.64	0.31	0.38	0.64	0.31	0.38	1.61
Tm	0.24	0.24	0.24	1.31	1.33	1.34	1.11	1.33	0.77	0.44	0.52	0.77	0.44	0.52	1.76
Yb	0.36	0.36	0.37	1.47	1.49	1.50	1.23	1.45	0.91	0.58	0.66	0.91	0.58	0.66	2.34
Lu	0.49	0.49	0.49	1.64	1.65	1.64	1.35	1.57	1.05	0.72	0.80	1.05	0.72	0.80	
<b>Ln<sup>+</sup> <math>5d^2 3f</math> valence substate:</b>															
La	3.32	3.31	3.31	4.37	4.36	4.36	4.60	4.89	3.77	3.77	4.21	3.77	3.77	4.21	5.58
Ce	3.44	3.42	3.43	4.54	4.51	4.52	4.72	5.00	3.88	3.89	4.32	3.88	3.89	4.32	5.54
Pr	3.57	3.55	3.56	4.72	4.70	4.71	4.86	5.14	4.02	4.02	4.46	4.02	4.02	4.46	5.64
Nd	3.71	3.70	3.71	4.92	4.90	4.91	5.00	5.28	4.17	4.17	4.61	4.17	4.17	4.61	5.83
Pm	3.87	3.84	3.85	5.13	5.11	5.12	5.14	5.42	4.31	4.32	4.76	4.31	4.32	4.76	6.15
Sm	4.02	3.99	4.00	5.35	5.33	5.34	5.29	5.56	4.47	4.48	4.92	4.47	4.48	4.92	6.38
Eu	4.19	4.16	4.17	5.59	5.57	5.57	5.42	5.70	4.65	4.65	5.10	4.65	4.65	5.10	6.73
Gd	4.36	4.34	4.34	5.82	5.82	5.82	5.64	5.91	4.83	4.83	5.28	4.83	4.83	5.28	7.14
Tb	4.53	4.51	4.51	6.07	6.06	6.06	5.80	6.08	5.01	5.01	5.46	5.01	5.01	5.46	7.42
Dy	4.71	4.69	4.69	6.33	6.31	6.31	6.00	6.26	5.20	5.20	5.65	5.20	5.20	5.65	7.69
Ho	4.90	4.87	4.87	6.59	6.57	6.57	6.16	6.44	5.39	5.39	5.84	5.39	5.39	5.84	7.92
Er	5.08	5.06	5.06	6.85	6.84	6.84	6.36	6.63	5.58	5.59	6.04	5.58	5.59	6.04	8.38
Tm	5.27	5.25	5.25	7.13	7.11	7.11	6.55	6.82	5.78	5.79	6.24	5.78	5.79	6.24	8.86
Yb	5.46	5.44	5.45	7.41	7.39	7.40	6.74	7.01	5.98	5.99	6.44	5.98	5.99	6.44	9.07
Lu	5.66	5.64	5.64	7.69	7.68	7.66	6.93	7.20	6.19	6.20	6.65	6.19	6.20	6.65	

$\text{Ln}^+ 5d^1 6s^1 3\text{D}$  valence substate:

La	4.30	4.30	4.30	4.50	4.50	5.07	5.30	5.04	5.20	5.65	5.30	5.52	5.26	5.42	5.89	5.81
Ce	4.36	4.35	4.35	4.57	4.56	5.12	5.35	5.10	5.25	5.71	5.37	5.59	5.33	5.48	5.96	5.83
Pr	4.41	4.41	4.41	4.64	4.62	5.17	5.40	5.16	5.31	5.77	5.43	5.65	5.40	5.55	6.03	5.89
Nd	4.46	4.46	4.45	4.70	4.69	5.22	5.45	5.21	5.36	5.82	5.50	5.73	5.48	5.63	6.11	6.09
Pm	4.51	4.50	4.50	4.77	4.76	5.26	5.50	5.26	5.41	5.87	5.57	5.79	5.55	5.70	6.18	
Sm	4.56	4.54	4.54	4.84	4.82	5.31	5.54	5.31	5.46	5.92	5.64	5.86	5.62	5.77	6.25	6.07
Eu	4.61	4.59	4.59	4.91	4.89	5.37	5.60	5.37	5.51	5.98	5.71	5.94	5.69	5.84	6.33	5.96
Gd	4.66	4.64	4.64	4.97	4.96	5.43	5.66	5.42	5.57	6.04	5.79	6.02	5.77	5.91	6.41	
Tb	4.71	4.69	4.68	5.04	5.02	5.47	5.70	5.47	5.61	6.09	5.86	6.08	5.84	5.98	6.48	6.23
Dy	4.75	4.73	4.73	5.11	5.09	5.53	5.76	5.52	5.67	6.14	5.94	6.16	5.92	6.06	6.56	6.31
Ho	4.80	4.78	4.77	5.18	5.16	5.57	5.80	5.57	5.71	6.19	6.02	6.25	5.99	6.13	6.64	
Er	4.84	4.83	4.82	5.25	5.24	5.62	5.86	5.63	5.77	6.25	6.10	6.33	6.07	6.21	6.72	6.54
Tm	4.89	4.87	4.87	5.33	5.31	5.68	5.91	5.68	5.82	6.30	6.18	6.41	6.15	6.29	6.80	6.61
Yb	4.94	4.92	4.91	5.40	5.38	5.73	5.96	5.73	5.87	6.35	6.27	6.50	6.23	6.37	6.88	6.70
Lu	4.98	4.96	4.96	5.48	5.46	5.78	6.01	5.78	5.92	6.40	6.36	6.59	6.32	6.45	6.97	6.89

$\text{Ln}^+ 6s^2 1\text{S}$  valence substate:

La	6.40	6.38	6.43	5.61	5.60	6.15	6.12	6.88	7.31	7.69	5.45	5.47	6.09	6.51	6.90	6.49
Ce	6.42	6.40	6.45	5.61	5.59	6.17	6.15	6.92	7.33	7.72	5.44	5.46	6.09	6.51	6.90	6.75
Pr	6.43	6.41	6.45	5.58	5.56	6.17	6.15	6.92	7.34	7.73	5.41	5.43	6.06	6.48	6.87	
Nd	6.41	6.39	6.43	5.54	5.52	6.15	6.14	6.91	7.32	7.71	5.36	5.39	6.02	6.44	6.83	
Pm	6.38	6.36	6.40	5.47	5.45	6.12	6.11	6.95	7.30	7.69	5.30	5.33	5.96	6.38	6.77	
Sm	6.34	6.32	6.36	5.40	5.38	6.09	6.08	6.84	7.26	7.65	5.23	5.26	5.89	6.31	6.70	
Eu	6.29	6.27	6.31	5.31	5.29	6.04	6.04	6.79	7.21	7.60	5.15	5.19	5.80	6.22	6.62	
Gd	6.23	6.21	6.25	5.21	5.20	6.00	6.00	6.74	7.16	7.55	5.07	5.11	5.72	6.14	6.54	6.15
Tb	6.16	6.14	6.18	5.11	5.10	5.93	5.93	6.67	7.09	7.42	4.97	5.01	5.62	6.04	6.43	6.56
Dy	6.09	6.07	6.11	5.00	4.99	5.87	5.88	6.60	7.02	7.42	4.87	4.91	5.51	5.93	6.32	6.53
Ho	6.01	5.99	6.02	4.88	4.87	5.78	5.78	6.52	6.94	7.33	4.76	4.81	5.39	5.81	6.20	
Er	5.92	5.90	5.94	4.76	4.75	4.78	4.78	6.44	6.85	7.25	4.65	4.70	5.27	5.68	6.08	6.06
Tm	5.83	5.81	5.84	4.63	4.62	4.64	4.64	6.35	6.76	7.16	4.53	4.58	5.14	5.55	5.95	6.10
Yb	5.73	5.72	5.75	4.49	4.49	4.51	4.51	6.25	6.67	7.07	4.41	4.47	5.00	5.42	5.81	6.03
Lu	5.63	5.62	5.65	4.36	4.35	4.38	4.38	6.16	6.57	6.98	4.31	4.37	4.87	5.28	5.68	5.43

**Table 7.** Excitation and ionization energies (eV); as Table 6, but additional optimized  $f$ -functions have been included in the basis set; CI(SD) [32, 40] and CEPA-1 [40] results are compared to experimental data [22] calculated from the lowest levels of each configuration; results specified in the second line for La refer to calculations with a  $4f$ -pseudopotential; all energies are with respect to the  $5d^1 6s^2 2D$  state

State	Ln	$0f$		$1f$		$2f$			Exp.	
		CEPA	CI(SD)	+Q	CEPA	CI(SD)	+Q	CEPA		
$5d^2 6s^1 4F$	La	0.83	0.24	0.43	0.53	0.14	0.33	0.45	0.33	
		0.84	0.17	0.35	0.47	0.10	0.27	0.39		
	Lu	2.66	2.30	2.50	2.52	2.15	2.34	2.41	2.34	
$5d^1 6s^1 3D$	La <sup>+</sup>	5.57	5.23	5.46	5.44	5.25	5.48	5.62	5.81	
		5.60	5.22	5.44	5.57	5.24	5.47	5.60		
	Lu <sup>+</sup>	6.61	6.27	6.50	6.55	6.25	6.49	6.58	6.89	
	$6s^2 1S$	La <sup>+</sup>	5.56	5.87	5.91	6.01	6.01	6.07	6.13	6.49
			5.58	6.02	6.09	6.13	6.11	6.19	6.23	
Lu <sup>+</sup>		4.51	4.59	4.66	4.82	4.83	4.92	4.99	5.43	
$5d^2 3F$	La <sup>+</sup>	5.98	5.28	5.53	5.60	5.21	5.44	5.60	5.58	
		5.99	5.17	5.40	5.53	5.15	5.38	5.52		
	Lu <sup>+</sup>	9.04	8.72	8.98	8.92	8.49	8.74	8.83	9.07	

$f$ -exponent 0.486) and Lu ( $4f^{14}$  subconfiguration;  $f$ -exponent 0.954), as well as for the  $5d^1 6s^1$  valence subconfiguration of La ( $4f^1$  subconfiguration;  $f$ -exponent 0.491) and Yb ( $4f^{14}$  subconfiguration;  $f$ -exponent 0.810). Further improvement is obtained by splitting the  $f$ -exponent into two exponents, where the splitting factor was optimized for the states indicated above ( $f$ -exponents: La 0.711, 0.260; Lu 1.406, 0.502 and La 0.720, 0.261; Yb 1.235, 0.413). Since CI(SD) results, corrected for size-consistency by means of Davidson's formula (+Q) [33], and results obtained from size-consistent CEPA-1 [39, 40] calculations are similar, we suspect that the largest part of the remaining errors might not be due to lacking size consistency but to neglect of triple excitations.

In order to investigate the effect of the  $f$ -pseudopotential on the CI-results we also performed calculations using a  $f$ -pseudopotential for La adjusted to the valence energies of the  $4f^1$  and  $5f^1$  one-valence-electron ion and thus admitting mixing of configurations with different  $4f$ -occupation. The results agree with those for a  $f$ -pseudopotential, adjusted to valence energies of the  $5f^1$  and  $6f^1$  one-valence-electron ion, to within 0.2 eV, cf. Table 7.

#### 4. Conclusion

The results presented in this paper for atoms and a forthcoming paper for molecules indicate that for the rare earth metals an inclusion of the partially occupied  $4f$ -orbitals in the core and the treatment of different  $f$ -occupations by

**Table 8.** Excitation and ionization energies (eV); as Table 7, but for the  $4f^1$  subconfiguration of La and the  $4f^{14}$  subconfiguration of Yb with respect to the  $6s^2 2S$  valence substate

Valence substate	$0f$		$1f$		$2f$		+Q	CEPA	Exp.
	CEPA	CI(SD)	CEPA	CI(SD)	CEPA	CI(SD)			
$5d^1 6s^1 \ ^3D$	La	1.74	1.30	1.44	1.48	1.21	1.33	1.37	1.02
	Yb	3.38	3.09	3.23	3.23	3.00	3.12	3.15	3.04
$5d^2 \ ^3F$	La	3.68	3.06	3.22	3.25	2.90	3.03	3.07	2.37
	Yb	6.87	6.51	6.65	6.60	6.32	6.45	6.46	5.88
$6s^2 \ ^1S$	La <sup>+</sup>	5.56	5.87	5.91	6.01	6.01	6.07	6.13	6.49
	Yb <sup>+</sup>	5.89	5.71	5.87	5.89	5.71	5.87	5.91	6.25
$5d^1 \ ^2D$	La <sup>+</sup>	6.44	5.88	6.08	6.10	5.81	5.99	6.04	5.75
	Yb <sup>+</sup>	9.24	8.83	9.02	8.99	8.69	8.86	8.90	9.10

different pseudopotentials offers the possibility of performing quantum chemical calculations on lanthanide compounds within a reasonable amount of computer time.

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