

The reliability of the small-core Lanthanide effective core potentials

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Abstract

The reliability of the small-core Lanthanide effective core potentials (ECP) is tested using MF and MF₃, for M=Eu, Gd, Tb, and Yb and the atomic excitation energies for Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb. In some case the ECP and all-electron (AE) results are in good agreement, while in others there are significant difference. The difference are much larger when the segmented basis set is used in conjunction with the ECP than when the atomic natural orbital (ANO) basis set is used. The study of the atoms suggests that problems for lanthanide containing molecules are associated with poor atomic excitation energies in the ECP treatment and even using the ANO basis set does not completely solve the problem. We note that the problem appears to be more severe for density functional approaches than for traditional correlation methods. We suggest that additional studies and new effective core potentials may be required for the Lanthanide atoms.

Keywords: effective core potentials, atomic excitation, atomization energy, and lanthanides

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I. INTRODUCTION

In recent work [1] on $\text{TiO}_x(\text{OH})_y$, we found that the geometries and harmonic frequencies computed using an B3LYP [2] hybrid [3] functional and coupled cluster single and doubles [4, 5], including a perturbational estimate of the triples [6], (CCSD(T)) approaches were in very good agreement, and even the computed reaction energies were in reasonable agreement. Thus optimizing the geometries and computing the frequencies at the B3LYP level and improving the energetics at the CCSD(T) level is a very cost effective approach. For the second transition row the inclusion of scalar relativistic effects during the geometry optimization become more important than for the first transition row. For all electron basis sets, including scalar relativistic effects adds the complication that analytic derivatives are not available in most codes. Switching to effective core potentials (ECPs) allows the inclusion of scalar relativistic effects and still have analytic first and second derivatives; in addition, using small core ECPs with correlation consistent basis sets in the CCSD(T) calculations yields accurate energetics. For example, we found that CCSD(T) reaction energies for $\text{YO}_x(\text{OH})_y$ and $\text{ZrO}_x(\text{OH})_y$ [7], using agreed with all-electron treatments (both using triple zeta basis sets) to within 1 kJ/mol for systems with only single bonds and 2-3 kJ/mol for systems with double bonds.

Given our success of using the B3LYP approach with an ECP to optimize the geometries and compute the harmonic frequencies for several species containing second and third transition row atoms, this is the approach we used in a recent study [8] of $\text{GdO}_x(\text{OH})_y$ and $\text{YbO}_x(\text{OH})_y$ species. The results for the $\text{YbO}_x(\text{OH})_y$ systems were consistent with our previous work, namely the B3LYP and Brueckner doubles [9] with triples (BD(T)) reaction energies were in reasonable agreement (a maximum difference of 23 kJ/mol). However, for $\text{GdO}_x(\text{OH})_y$ the difference between the B3LYP and BD(T) levels increased with number of bonds, so that while GdOH shows reasonable agreement between the B3LYP ECP and BD(T) AE treatments, $\text{Gd}(\text{OH})_3$ shows a 248 kJ/mol difference between the B3LYP/TZ ECP and the BD(T)/QZ AE calculations. If an all electron treatment is used in the B3LYP calculations, the difference between the B3LYP/TZ AE and BD(T)/QZ AE calculations is reduced to 2.6 kJ/mol. These results suggest that the Gd ECP is not performing as well as hoped. In this work we report on some additional tests of Lanthanide atoms and molecules to assess if the problem encountered for Gd is unique or if other atoms are similarly affected.

We study EuF, EuF₃, GdF, GdF₃, TbF, TbF₃, YbF, and YbF₃. We also look at the energy levels of Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb atoms.

II. METHODS

The MF and MF₃, for M=Eu, Gd, Tb, and Yb, geometries are optimized and harmonic frequencies computed using the B3LYP hybrid functional. The metal atoms are described with both ECP and all-electron treatments. The metal ECPs include the inner most 28 electrons in the ECP [10] and explicitly include the 4f electrons in the valence space. The (14s13p10d8f6g)/[10s8p5d4f3g] segmented and (14s13p10d8f6g)/[6s6p5d4f3g] atomic natural orbital (ANO) basis sets [11, 12] are used; the calculations are denoted ECP(seg) and ECP(ANO), respectively. In the all-electron calculations, metal atoms use the Douglas-Kroll correlation consistent polarized weighted core valence triple zeta basis sets of Lu and Peterson [13], i.e. the cc-pwCVTZ-DK3 set and the F uses the aug-cc-pVTZ set of Dunning and coworkers [14, 15]. In the AE calculations, the scalar relativistic effects are included using second order Douglas-Kroll-Hess (DKH) method [16], which results in the AE frequencies being computed using only energy differences. In order to eliminate imaginary frequencies and bring the two components of the e vibrations into agreement, we use a superfine grid, four displacements instead of the default two, and a larger step size, i.e. freq=(step=500,fourpoint) in Gaussian16 [17].

CCSD(T) calculations are performed using two approaches: in the first, all of the orbitals are taken from the HF calculations and, in the second, the core orbitals are taken from the HF and the valence and virtual orbitals are taken from the B3LYP calculations [18], denoted B3-CCSD(T). The same basis sets are used as were used in the DFT calculations. In the AE calculations the third order DKH approach is used to include scalar relativistic effects. The metal 4f, 5s, 5p, 5d, and 6s electrons and the F 2s and 2p electrons are correlated in the CCSD(T) calculations. The CCSD(T) calculations are performed using Molpro [19].

The atomic energy levels are studied using the spin restricted Hartree-Fock, with and without symmetry and equivalence restrictions, the B3LYP, and the CCSD(T) levels of theory. The cc-pwCVQZ-DK3 basis sets [13] are used in the atomic calculations. In the AE calculations, the third order DKH approach is used to include scalar relativistic effects. The metal 4f, 5s, 5p, 5d, and 6s electrons are correlated in the CCSD(T) calculations. All of the

atomic calculations were performed with Molpro [19].

The spin-orbit splitting is quite large for these systems; in some cases, the order of the states reverse between the lowest spin-orbit level and the m_j averaged energies. When all the spin-orbit levels are available from experiment, we use experiment [20]. When there are missing spin-orbit levels, we use theory to compute the missing levels. This is done using the state interaction approach with the Breit-Pauli Hamiltonian, where the orbitals are determined using the state-averaged complete active space self consistent field (SA-CASSCF) approach. The specific choice of active space and states included in the SA-CASSCF and the configuration interaction calculations in the state-interaction approach are discussed below and/or given in the Supplemental Information.

III. RESULTS

A. MF and MF₃

The results of the MF calculations are summarized in Table I. The computed D_e values are converted to D_0 values using the computed ω_e values and experimental spin-orbit splittings (the difference between the lowest m_j level and the weighted average of the m_j levels.) The AE and ECP approaches yield the same ground state. The agreement between the ECP and AE treatments for D_0 , r_e , and ω_e values is good for EuF and YbF. For GdF and TbF, the ECP(seg) harmonic frequencies are smaller than the AE results. Using the ECP(ANO) basis set brings the GdF ω_e value into good agreement with the AE result, while for TbF it improves the agreement, but the ECP(ANO) value is still smaller. For TbF, the ECP(ANO) increases the D_0 disagreement with the AE value. There is limited experimental data [21], and there is reasonable agreement between theory and experiment. The AE and ECP(Seg) Mulliken population are given in the Supplemental Information Tables S1-S4. The largest difference is for TbF, where the AE $f\sigma$ population is 0.2 electrons larger than the ECP(seg) population. While it is tempting to attribute that difference between the AE and ECP(seg) results to this change in the population, the ECP(Seg) for GdF also yields a longer r_e and smaller ω_e than the AE, but the AE and ECP(seg) populations are more similar than those for TbF.

The results for XF₃ species are given in Tables II and III along with the limited ex-

perimental data [22, 23]. The populations are in Tables S5-S8. We have included both components of the e vibrations, which differ slightly for the AE treatment due to the use of numerical differences for the calculation of the harmonic frequencies. The small differences for the AE treatment supports the use of the larger displacements and 4 displacements, as the defaults show larger difference. We also note that using this same numerical approach for the ECP(seg) approach shows a maximum difference with the analytic approach of 1.2 cm^{-1} . There are also small differences for some of the ECP(ANO) calculations even though analytic derivatives are used.

We first note that there is good agreement with the limited experimental results for all three treatments. Comparing the three levels of theory among themselves shows that the ECP(seg), ECP(ANO), and AE results for EuF_3 and YbF_3 are very similar. For GdF_3 , the ECP(seg) atomization energy differs with the AE by 2.3 eV and the lowest frequency by 50.9 cm^{-1} . The ECP(ANO) reduces the difference with the AE treatment for the atomization energy and the lowest frequencies. While the lowest frequency at the ECP(seg) level is actually in better agreement with experiment than the AE approach, we suspect that this is fortuitous. All three treatments are similar for TbF_3 except for the atomization energy, where the ECP(ANO) value is larger than the other two results. This is similar to TbF , where the ECP(ANO) yielded a somewhat larger binding energy than the other two treatments.

The results for the XF_3 suggests that the ECP(seg) treatment is not as reliable as either AE or ECP(ANO) treatments at the B3LYP level. We next compute the GdF_3 atomization energy using the CCSD(T) approach at the B3LYP optimized geometry to see if the problem with the ECP(seg) is unique to B3LYP or if it also occurs for other highly correlated methods. The results are summarized in Table III, the B3LYP results from Table II are included for comparison. The CCSD(T) atomization energy using the AE treatment is 18.91 eV compared with 18.68 eV for the ECP(ANO) treatment, which is good agreement. This is in contrast with the ECP(seg) case where the CCSD fails. The results for the B3-CCSD(T) approach show the same agreement for the AE and ECP(ANO) treatments and again the ECP(seg) CCSD fails. The B3LYP and CCSD(T) results suggests that the problems with the ECP(seg) treatment can be largely avoided by using the ANO basis set instead of the segmented basis set. However, as we show below for the atomic energy levels there are cases where the use of either the segmented or the ANO basis sets leads to failure.

B. Atomic calculations

The spin-orbit splitting in the Lanthanides is sufficiently large that it must be accounted for before comparing theory with experiment. For the ground states of all atoms that we consider in this work, and for excited states of Pr, Nb, Eu, Gd, Tb, and Dy, the spin-orbit levels can clearly be attributed to the splitting of a specific LS state. For the excited states of Ho, Er, Tm, and Yb, this is not the case. We therefore break our discussion in two cases. The results for Pd, Nb, and Eu are given in Table IV. The results for Gd, Tb, and Dy, which are similar, are given in supplemental data Tables S9 and S10. For the ground states, the SA-CASSCF calculation is performed including all components of the LS state; this corresponds to a symmetry and equivalence restricted SCF calculation. The m_j levels are computed in a state interaction calculation including all of the LS components. For the excited states, SA-CASSCF are performed for the states listed in the tables, in most cases this is one state, while for a few, two near by states are included. The theoretical values for the excited states are shifted so that the lowest m_j component agrees with experiment. Overall the agreement of theory and experiment is very reasonable.

Ho is representative of the second class of atoms and the spin orbit levels are shown in Table V. The results for the ground $^4I^o$ state are consistent with those for Pr to Dy, namely the levels appear to be derived from a specific LS state. The lowest excited LS state is the 6I and the computed m_j levels show no correspondence to experiment. The calculations are repeated adding one LS state at a time. When all of the quartet sextet states arising from the coupling of the shell 5d with the $4f^{10}(^4I_4)$ shell are included in the calculation, the agreement between theory and theory is acceptable. Adding an equal number of quartet states as sextet states makes a small improvement. The results of the calculations suggest that the lowest spin-orbit component is derived from the 6I state.

We next compute the excitation energies between the ground and lowest excited state at the HF, B3LYP, CCSD(T), and B3-CCSD(T) levels of theory using the all electron and ECP approaches; the results are summarized in Table VI. To compare with experiment we need to account for the experimental spin orbit splittings. For the states that clearly arise from the splitting of one LS state, we perform a weighted average of the experimental m_j energies. In those cases where there are missing experimental lines, the theoretical values are used, for example theory is used for Pr 4I $m_j=15/2$ level. As noted above, the excited

states of Pr, Nb, Eu, Gd, Tb, and Dy are not derived from a single LS state. For these cases, we shift the lowest observed line by the difference in energy between our lowest m_j component and our lowest LS state included in the spin orbit calculation. We compare our computed LS separations with these "corrected" experimental values.

For the AE treatment, the CCSD(T) and B3-CCSD(T) results are in good agreement with each other and in good agreement with experiment. The ECP(seg) results vary significantly. For Pr, Nd, Ho, Er, Tm, and Yb the AE and ECP(seg) results show good agreement. For Eu, the HF based CCSD(T) shows agreement between the AE and ECP(seg), but the B3LYP and B3-CCSD(T) results are in poor agreement. For Gd, Tb, and Dy, the ECP(seg) B3LYP results show very poor agreement with the AE results and the B3-CCSD(T) calculations fail. We assume that the very poor results for the ECP(seg) treatment of Gd are related to the problems observed in GdF₃. Tb also shows poor results and the only indication of a problem in the molecular results was the slightly poorer agreement of the r_e value for TbF and an $4f_{\sigma}$ population that shows some differences between the AE and ECP(seg) treatment. We also note that while we did not see any indication of a problem with EuF or EuF₃, the Eu atom results show some significant differences between the AE and ECP(seg) treatments, but not as bad as for Gd or Tb.

Given that the worst agreement between the AE and ECP(seg) results occur for Gd, Tb, and Dy, we consider the ECP(ANO) for these three cases. For Gd, the HF-sym and HF results are very similar for the ECP(ANO) and ECP(seg) results. The ECP(ANO) and ECP(seg) CCSD(T) results are in good mutual agreement and in reasonable agreement with the AE results and with experiment. At the B3LYP level, the ECP(ANO) is in much better agreement with the AE than the ECP(seg). The B3-CCSD(T), which failed for the ECP(seg), yields a ECP(ANO) separation in good agreement with the AE results. Thus for Gd, switching to the ECP(ANO) basis set results in good agreement with the AE result; this is similar to the XF₃ results described above. For Tb and Dy, we again find the HF and HF-sym results to be very similar for the ECP(seg) and ECP(ANO) approaches, and to be in good agreement with the AE results. Unlike Gd, the CCSD(T) fails for Tb and Dy for both the ECP(ANO) and ECP(seg) approaches. For the B3LYP, the ECP(ANO) is a significant improvement over the ECP(seg) separation, but unlike Gd, the difference with the AE results is still quite large. The B3-CCSD(T) fails for both the ECP(ANO) and ECP(seg) approaches. The Tb and Dy results show that even using the ECP(ANO)

approach does not solve all of the problems encountered using the ECP(seg) approach.

IV. CONCLUSIONS

We have studied EuF, EuF₃, GdF, GdF₃, TbF, TbF₃, YbF, and YbF₃ and the excitation energies of Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb atoms. In many cases we find good agreement between the all-electron and ECP treatments, while in others the agreement is less than satisfactory. We find that in many of the cases using the ANO basis set instead of the segmented basis set avoids the ECP problem. However, there are cases where even using ANO does not avoid problems associated with the ECP treatment. We suggest that additional studies and new effective core potentials may be required for the Lanthanide atoms.

V. ACKNOWLEDGMENTS

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- [1] Nguyen Q, Bauschlicher CW, Myers DL, Jacobson NS, Opila EJ (2017) Computational and Experimental Study of Thermodynamics of the Reaction of Titania and Water at High Temperatures. *J. Phys. Chem. A* 121:9508-9517.
 - [2] Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) Ab initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields *J. Phys. Chem.* 98:11623-11627.
 - [3] Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange *J. Chem. Phys.* 98:5648-5652.
 - [4] Bartlett RJ (1981) Many-body perturbation theory and coupled cluster theory for electron correlation in molecules. *Annu. Rev. Phys. Chem.* 32:359-401.
 - [5] Knowles PJ, Hampel C, Werner H-J (1993) Coupled cluster theory for high spin, open shell reference wave functions. *J. Chem. Phys.* 99:5219-5227. (See also (2000) Erratum: Coupled cluster theory for high spin, open shell reference wave functions, *J. Chem. Phys.* 112:3106-3107.

- [6] Raghavachari K, Trucks GW, Pople JA, Head-Gordon MA (1989) A fifth-order perturbation comparison of electron correlation theories. *Chem. Phys. Lett.* 157:479-483.
- [7] Bauschliche, CW, Bodenschatz C, Myers DL, Jacobson, NS (2020) Thermodynamics of high-temperature aluminum, zirconium, and yttrium hydroxide and oxyhydroxide vapor species. *J. Am. Ceram. Soc.* 103:5870–5880.
- [8] Bauschlicher CW, Jacobson NS (2021) Thermochemistry of Ytterbium and Gadolinium Hydroxides and Oxy-Hydroxides *J. Phys. Chem. A.* 125:2913-2922
- [9] Dykstra CE (1977) Examination of Brueckner condition for selection of molecular-orbitals in correlated wavefunctions, *Chem. Phys. Lett.* 45:466-69.
- [10] Dolg M, Stoll H, Preuss H (1989) Energy-adjusted ab initio pseudopotentials for the rare earth elements, *J. Chem. Phys.*, 90:1730-1734.
- [11] Cao X, Dolg, M (2002) Segmented contraction scheme for small-core lanthanide pseudopotential basis sets, *J. Molec. Struct. Theochem.*, 581:139-147.
- [12] Cao, X. Dolg, M (2001) Valence basis sets for relativistic energy-consistent small-core lanthanide pseudopotentials, *J. Chem. Phys.* 115:7348.
- [13] Lu Q, Peterson KA (2016) Correlation consistent basis sets for lanthanides: The atoms La–Lu *J. Chem. Phys.*, 145:054111.
- [14] Dunning TH (1989) Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen, *J. Chem. Phys.* 90:1007-1023.
- [15] Woon DE, Dunning TH (1993) Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon, *J. Chem. Phys.* 98:1358-1371
- [16] Wolf A, Reiher M, Hess BA (2002) *J. Chem. Phys.* 117:9215.
- [17] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, et al. (2016) Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT
- [18] Fang Z, Lee Z, Peterson KA, Dixon DA (2016) Use of Improved Orbitals for CCSD(T) Calculations for Predicting Heats of Formation of Group IV and Group VI Metal Oxide Monomers and Dimers and UCl 6. *Journal of Chemical Theory And Computation* 12,:583–3592.
- [19] Werner H-J, Knowles PJ, Knizia G, Manby FR, Schütz M, Celani P, Györffy W, Kats D, Korona,T, Lindh R, et al. MOLPRO, version 2015.1, a package of ab initio programs, see <http://www.molpro.net>. N.b. some of the spin-orbit calculations were performed using an old

version, since we had the source and could increase the dimensions required for the larger spin orbit calculations.

- [20] https://physics.nist.gov/PhysRefData/Handbook/atomic_number.htm
- [21] Huber KP, Herzberg G. (1979) Molecular Spectra and Molecular Structure: IV Constants of Diatomic Molecules. Van Nostrand Reinhold Company, New York.
- [22] Hauge RH, Hastie JW, Margrave JL (1971) Force Constants and Geometries of matrix isolated rare-earth trifluorides, Journal of the Less-Common Metals, 23:359 - 365
- [23] Hastie JW, Hauge RH, Margrave JL (1975), Geometries and entropies of metal trifluorides from infrared spectra: ScF₃, YF₃, LaF₃, CeF₃, NdF₃, EuF₃, and GdF₃, Journal of the Less-Common Metals, 39:309 - 334

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Ethics declarations

Conflict of interest

The author declare no conflicts of interests.

TABLE I: Summary of the B3LYP calculations on MF, for M= Eu, Gd, Tb, and Yb.

Mol	Basis	D ₀ ^a	r _e ^b	ω _e ^c	Ground state and occupation
EuF	ECP(Seg)	5.54	2.089	483.2	⁹ Σ ⁻ σ ¹ σ ¹ π ² δ ² φ ²
	ECP(ANO)	5.54	2.090	482.1	
	AE	5.63	2.085	485.5	
	AE-ECP(Seg)	0.08	-0.004	2.3	
	AE-ECP(ANO)	0.08	-0.005	3.4	
	HH ^d	5.42			
GdF	ECP(Seg)	6.36	1.997	556.4	⁸ Σ ⁻ σ ¹ π ² δ ² φ ²
	ECP(ANO)	6.43	1.960	601.6	
	AE	6.46	1.968	596.1	
	AE-ECP(Seg)	0.10	-0.029	39.7	
	AE-ECP(ANO)	0.03	0.008	-5.5	
	HH ^d	6.08			
TbF	ECP(Seg)	6.23	2.020	530.0	⁷ Δ σ ¹ π ² δ ¹ φ ²
	ECP(ANO)	6.52	1.997	545.3	
	AE	6.18	1.969	570.7	
	AE-ECP(Seg)	-0.05	-0.051	40.7	
	AE-ECP(ANO)	0.34	-0.028	25.4	
	HH ^d				
YbF	ECP(Seg)	5.12	2.030	489.5	² Σ ⁺ σ ¹
	ECP(ANO)	5.11	2.030	487.1	
	AE	5.04	2.015	491.7	
	AE-ECP(Seg)	-0.08	-0.015	2.2	
	AE-ECP(ANO)	-0.07	-0.015	4.6	
	HH ^d	4.8	2.016	501.9	

^a Dissociation energy in eV, including the computed zero-point energy and the effect of spin-orbit splitting.

^b Bond lengths are in Å.

^c Vibrational frequencies are in cm⁻¹.

^d Value taken from Huber and Herzberg [21].

TABLE II: Summary of the B3LYP calculations on MF₃, for M= Eu, Gd, Tb, and Yb.

Mol	Basis	D ₀ ^a	r(M-F) ^b	angle ^c	ω_e^d					
					a ₁	e	e	e	e	a ₁
EuF ₃	ECP(Seg)	15.43	2.044	13.9	82.6	136.4	136.4	524.1	524.1	556.2
	ECP(ANO)	15.45	2.045	13.8	82.6	136.2	136.2	524.2	524.3	555.9
	AE	15.74	2.044	14.2	84.5	136.5	137.4	523.8	523.9	556.2
	AE-ECP(Seg)	0.32	0.000	0.3	1.9	0.1	1.0	-0.3	-0.2	0.0
	AE-ECP(ANO)	0.29	-0.001	0.4	1.9	0.2	0.2	-0.4	-0.4	0.3
	Expt ^e				90±14	120±10		544±10		572±10
	Expt ^f				89	133		529.7		544.9
GdF ₃	ECP(Seg)	16.75	2.024	18.8	100.6	145.9	145.9	530.5	530.5	558.2
	ECP(Seg) ^g				101.7	148.1	150.5	531.3	531.9	558.9
	ECP(ANO)	18.61	2.033	14.5	72.5	132.8	133.0	536.1	537.4	565.3
	AE	19.05	2.043	9.9	49.7	131.6	132.2	534.2	534.3	556.1
	AE-ECP(Seg)	2.31	0.019	-8.9	-50.9	-14.3	-13.7	3.7	3.8	-2.1
	AE-ECP(ANO)	0.44	0.010	4.6	-22.8	-1.2	-0.8	-1.9	-3.1	-9.2
	Expt ^e				95±15	130±10		552±10		583±10
	Expt ^f				94	138		537.5		560.4
TbF ₃	ECP(Seg)	18.80	2.018	9.5	67.2	136.3	136.4	545.8	545.9	563.4
	ECP(ANO)	19.12	2.002	11.5	72.6	133.6	133.6	532.0	532.0	579.8
	AE	18.63	2.027	12.8	72.2	132.3	133.4	537.2	537.4	565.3
	AE-ECP(Seg)	-0.17	0.019	3.3	5.0	-4.0	-3.0	-8.6	-8.4	1.9
	AE-ECP(ANO)	-0.49	-0.025	1.3	-0.4	-1.3	-1.2	5.2	5.4	-14.5
	Expt ^f							540.1		566.7
YbF ₃	ECP(Seg)	15.90	1.983	6.4	61.4	141.3	141.9	556.2	556.2	578.8
	ECP(ANO)	15.97	1.983	6.0	61.0	140.8	141.4	556.6	556.7	578.2
	AE	15.83	1.981	9.6	66.6	144.7	144.9	556.7	556.7	580.0
	AE-ECP(Seg)	-0.08	-0.002	3.2	5.2	3.4	3.0	0.5	0.5	1.2
	AE-ECP(ANO)	-0.14	-0.002	3.6	5.6	3.9	3.5	0.1	0.0	1.8
	Expt ^f				100	144		564.7		584.1

^a Atomization energy in eV; includes zero-point energy and the effect of spin-orbit splitting.

^b Bond lengths are in Å.

^c The out of plane angle.

^d Vibrational frequencies are in cm⁻¹.

^e Estimated gas-phase value from Hastie et al [23].

^f Ne matrix values from Hauge et al. [22].

^g The frequencies are computed numerically using the same parameters as used for the AE calculations.

TABLE III: Summary of the computed atomization energies for GdF_3 .

Calculation	Basis	Atomization energy (eV)
B3LYP	ECP(Seg)	16.75
B3LYP	ECP(ANO)	18.61
B3LYP	AE	19.05
CCSD(T)	ECP(Seg)	Failed
CCSD(T)	ECP(ANO)	18.68
CCSD(T)	AE	18.91
B3-CCSD(T)	ECP(Seg)	Failed
B3-CCSD(T)	ECP(ANO)	18.75
B3-CCSD(T)	AE	18.95

TABLE IV: Summary spin-orbit splitting, in cm^{-1} .

Pr								
$^4I^o(3, 0, 2)^a$			$^4I(2, 1, 2)$			$^4K(2, 1, 2)$		
m_j	Exp	Calc	m_j	Exp	Calc ^b	m_j	Exp	Calc ^b
4.5	0.0	0.0	4.5	4432.2	4432.2	5.5	4866.5	4866.5
5.5	1376.6	1302.1	5.5	6313.2	5859.1	6.5	6603.6	6541.6
6.5	2846.8	2841.2	6.5	7951.3	7545.1	7.5	8363.9	8474.9
7.5	4381.1	4617.3	7.5	9489.7 ^c	9489.7	8.5	10666.3 ^c	10666.3
Avg	2486.1	2432.1		7155.7	7369.9		7959.5	7944.4
Δ	0.0	0.0		4669.6	4937.8		5473.4	5512.3
Nd								
$^5I(4, 0, 2)$			$^5L^o(3, 1, 2)$			$^5K^o(3, 1, 2)$		
4.0	0.0	0.0	6.0	6764.2	6764.2	5.0	6854.0	6854.0
5.0	1128.1	1029.9	7.0	8402.5	8318.0	6.0	8411.9	8201.9
6.0	2366.6	2267.0	8.0	10160.6	10094.1	7.0	10017.8	9772.8
7.0	3681.7	3709.8	9.0	12162.1	12093.1	8.0	11704.6	11567.3
8.0	5048.6	5358.9	10.0	14316.4 ^c	14316.4	9.0	13585.0 ^c	13585.0
Avg	2885.4	2834.2		10761.4	10805.0		10444.9	10561.5
Δ	0.0	0.0		7876.0	7970.8		7559.6	7727.2
Eu								
$^5I(7, 0, 2)$			$^{10}D^o(7, 1, 1)$					
3.5	0.0	0.0	2.5	12923.7	12923.7			
			3.5	13048.9	13114.4			
			4.5	13222.0	13359.7			
			5.5	13457.2	13659.4			
			6.5	13778.7	14013.6			
Avg	0.0	0.0		13523.2	13370.8			
Δ	0.0	0.0		13523.2	13370.8			

^a The state is followed by the number of 4f, 5d, and 6s electrons.

^b Lowest m_j level shifted to agree with experiment.

^c Experimental level is missing, theory is used instead.

TABLE V: Summary Ho spin-orbit splitting, in cm^{-1} .

$^4I^0(11,0,2)$ ground state									
m_j	theory	expt							
15/2	0	0.0							
13/2	5244	5419.7							
11/2	9790	8605.2							
9/2	13635	10695.8							
m_j	excite states (10,1,2) ^a						expt		
	6I	$+^6K$	$+^6H$	$+^6L$	$+^6G$	+quartets	$(8,\frac{3}{2})$	$(8,\frac{5}{2})$	$(7,\frac{3}{2})$
17/2	0	0	0	0	0	0	0.0		
15/2	3438	3107	405	438	438	37	48.2		
13/2	6472	6070	3580	3611	1349	1275	768.2		
19/2		2133	2133	1732	1732	1724	1362.6		
21/2				3653	3653	4005	2943.4		
17/2		6020	6020	5389	5389	4289	3151.6		
13/2		11783	7964	7903	4450	4307			3965.6
15/2		9199	4444	4403	4403	4384	3960.1		
19/2				7114	7114	4603	3310.9		
11/2	9101	8840	6693	6727	5182	5187			4704.0
17/2				10115	10115	7288			6751.4
15/2			9309	8629	8629	7869			6757.1
13/2			11998	11417	8181	7973			
11/2		13821	10893	10858	8085	8078	8558.5		
17/2						8845			
9/2	11326	11408	9662	9702	8656	8858			
19/2						9220			

^a The orbitals are optimized for a SA-CASSCF including all of the sextet states shown.

TABLE VI: Summary Atomic energy levels, in cm^{-1} .

	Pr		Nd		Eu		Gd		
Lower ^a	⁴ <i>I</i> ^o (2, 0, 2)		⁵ <i>I</i> (4, 0, 2)		⁸ <i>S</i> (7, 0, 2)		⁹ <i>D</i> ^o (7, 1, 2)		
Upper	⁴ <i>I</i> (2, 1, 2)		⁵ <i>L</i> ^o (3, 1, 2)		¹⁰ <i>D</i> ^o (7, 1, 1)		¹¹ <i>F</i> (7, 2, 1)		
	AE	ECP	AE	ECP	AE	ECP	AE	ECP	
	seg		seg		seg		seg ANO		
HF-sym ^b	-925	-688	-2165	-1911	9756	11529	720	1323	1332
HF	-79	125	1138	2042	9602	11413	779	1343	1269
CCSD(T)	2974	2674	6325	6296	13281	15090	6306	7093	7063
B3LYP	11433	13832	14461	16069	11684	32048	5027	-12753	7584
B3-CCSD(T)	3031	1800	6401	5897	13283	33683	6334	Fail	7103
EXPT	4670		7560		11661		6624		
	Tb		Dy		Ho		Er		
Lower	⁶ <i>H</i> ^o (9, 0, 2)		⁵ <i>I</i> (10, 0, 2)		⁴ <i>I</i> ^o (11, 0, 2)		³ <i>H</i> (12, 0, 2)		
Upper	⁸ <i>G</i> (8, 1, 2)		⁷ <i>H</i> ^o (9, 1, 2)		⁶ <i>I</i> (10, 1, 1)		⁵ <i>G</i> ^o (11, 1, 2)		
	AE	ECP	AE	ECP	AE	ECP	AE	ECP	
	seg ANO		seg ANO		seg		seg		
HF-sym	-26538	-25415	-25658	-17547	-16369	-16720	-17586	-16797	-20079 -18981
HF	-26646	-25496	-25720	-15321	-13991	-14317	-15881	-14753	-18000 -16917
CCSD(T)	-4661	Fail	Fail	6632	Fail	Fail	9011	7894	9240 7795
B3LYP	4343	-59252	-11261	12062	50763	4037	13446	15797	12722 12848
B3-CCSD(T)	-4243	Fail	Fail	7690	Fail	Fail	9711	9229	10066 8810
EXPT	-3514		5836		10040		10803		
	Tm		Yb						
Lower	² <i>F</i> ^o (13, 0, 2)		¹ <i>S</i> (14, 0, 2)						
Upper	⁴ <i>F</i> (12, 1, 2)		³ <i>P</i> (13, 1, 2)						
	AE	ECP	AE	ECP					
	seg		seg						
HF-sym	-13803	-12689	-476	-560					
HF	-8046	-6672	1213	3609					
CCSD(T)	19674	18737	29968	29253					
B3LYP	19728	22111	27904	31412					
B3-CCSD(T)	20769	19500	29864	29502					
EXPT	17035		28001						

^a The state is followed by the number of 4f, 5d, and 6s electrons.

^b Symmetry and equivalence restrictions are imposed.

TABLE S1: Summary EuF Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha\text{-}\beta$	Tot	α	β	$\alpha\text{-}\beta$
Eu s	10.82	5.82	5.00	0.82	0.05	-0.01	0.00	0.06
p σ	8.06	4.06	4.00	0.06	-0.04	-0.02	-0.02	-0.00
p π	16.01	8.01	8.00	0.00	-0.00	-0.00	-0.00	-0.00
p tot	24.07	12.07	12.00	0.07	-0.04	-0.02	-0.02	-0.00
d σ	4.20	2.15	2.05	0.10	-0.03	-0.02	-0.01	-0.01
d π	8.13	4.08	4.05	0.03	0.01	0.00	0.00	-0.00
d δ	8.00	4.00	4.00	0.00	0.00	0.00	-0.00	0.00
d tot	20.33	10.23	10.11	0.12	-0.02	-0.02	-0.01	-0.01
f σ	1.00	0.99	0.01	0.98	-0.00	-0.00	-0.00	0.00
f π	2.00	1.99	0.01	1.98	0.01	0.00	0.00	-0.00
f δ	2.00	2.00	0.00	2.00	0.00	0.00	0.00	0.00
f ϕ	2.00	2.00	0.00	2.00	0.00	0.00	0.00	0.00
f tot	7.00	6.98	0.02	6.96	0.00	0.00	0.00	0.00
Total	62.23	35.10	27.13	7.97	-0.02	0.02	-0.03	0.05
F s	4.02	2.02	2.00	0.02	0.03	0.03	0.00	-0.02
p σ	1.90	0.96	0.94	0.02	-0.00	-0.02	0.02	-0.03
p π	3.84	1.91	1.93	-0.01	-0.01	-0.00	-0.01	0.01
p tot	5.74	2.87	2.87	0.01	-0.01	-0.02	0.01	-0.03
Total	9.77	4.90	4.87	0.03	0.02	-0.02	0.03	-0.05

TABLE S2: Summary GdF Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha-\beta$	Tot	α	β	$\alpha-\beta$
Gd s	11.60	5.79	5.81	-0.02	0.12	0.06	0.00	0.00
p σ	8.08	4.03	4.05	-0.02	-0.06	-0.02	-0.04	0.01
p π	16.01	8.00	8.00	0.00	-0.00	-0.00	-0.00	-0.00
p tot	24.09	12.03	12.05	-0.02	-0.06	-0.02	-0.04	0.01
d σ	4.32	2.19	2.14	0.05	-0.01	0.01	-0.02	0.02
d π	8.16	4.09	4.07	0.02	0.01	0.01	0.01	-0.00
d δ	8.00	4.00	4.00	0.00	-0.00	0.00	-0.00	-0.00
d tot	20.48	10.28	10.21	0.07	0.00	0.01	-0.01	0.02
f σ	1.02	1.00	0.02	0.98	0.02	-0.00	0.03	-0.03
f π	2.02	2.00	0.02	1.99	0.01	0.00	0.01	-0.01
f δ	2.00	2.00	0.00	2.00	0.00	0.00	0.00	0.00
f ϕ	2.00	2.00	0.00	2.00	0.00	0.00	0.00	0.00
f tot	7.04	7.00	0.03	6.97	0.03	-0.00	0.03	-0.03
Total	63.22	35.11	28.11	7.00	0.08	0.04	0.04	0.01
F s	4.08	2.05	2.03	0.02	-0.02	0.00	0.00	-0.02
p σ	1.89	0.94	0.95	-0.01	-0.04	-0.02	-0.03	0.01
p π	3.80	1.90	1.90	-0.01	-0.02	-0.01	-0.01	0.01
p tot	5.69	2.83	2.86	-0.02	-0.06	-0.02	-0.04	0.02
Total	9.78	4.89	4.89	0.00	-0.08	-0.04	-0.04	-0.01

TABLE S3: Summary TbF Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha\text{-}\beta$	Tot	α	β	$\alpha\text{-}\beta$
Tb s	11.65	5.84	5.81	0.03	-0.04	-0.07	0.00	0.09
p σ	8.09	4.02	4.07	-0.05	-0.07	-0.01	-0.06	0.05
p π	16.01	8.01	8.00	0.00	-0.00	-0.00	-0.00	-0.00
p tot	24.10	12.03	12.07	-0.05	-0.07	-0.01	-0.06	0.05
d σ	4.25	2.14	2.11	0.03	0.01	0.04	-0.03	0.06
d π	8.15	4.08	4.07	0.01	0.02	0.01	0.01	-0.00
d δ	8.00	4.00	4.00	-0.00	-0.00	-0.00	-0.00	0.00
d tot	20.40	10.22	10.18	0.04	0.03	0.05	-0.02	0.06
f σ	1.01	1.00	0.01	0.99	0.19	-0.00	0.19	-0.20
f π	2.01	2.00	0.01	1.99	0.01	0.00	0.01	-0.01
f δ	3.00	2.00	1.00	1.00	0.00	0.00	0.00	-0.00
f ϕ	2.00	2.00	0.00	2.00	0.00	0.00	0.00	0.00
f tot	8.03	7.00	1.03	5.98	0.20	-0.00	0.20	-0.20
Total	64.18	35.09	29.09	6.00	0.11	0.05	0.06	-0.00
F s	4.07	2.05	2.03	0.02	-0.02	-0.00	0.00	-0.02
p σ	1.91	0.95	0.96	-0.02	-0.06	-0.02	-0.04	0.02
p π	3.82	1.91	1.91	-0.00	-0.03	-0.01	-0.02	0.01
p tot	5.73	2.85	2.87	-0.02	-0.09	-0.03	-0.06	0.02
Total	9.82	4.91	4.91	0.00	-0.11	-0.05	-0.06	0.00

TABLE S4: Summary YbF Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha\text{-}\beta$	Tot	α	β	$\alpha\text{-}\beta$
Yb s	10.86	5.81	5.05	0.75	0.12	0.03	0.00	0.07
p σ	8.09	4.10	4.00	0.10	-0.05	-0.04	-0.01	-0.03
p π	16.02	8.01	8.01	0.00	-0.00	-0.00	-0.00	-0.00
p tot	24.11	12.10	12.00	0.10	-0.05	-0.04	-0.01	-0.03
d σ	4.15	2.10	2.05	0.05	-0.01	-0.00	-0.00	0.00
d π	8.13	4.06	4.06	0.00	0.01	0.00	0.01	-0.00
d δ	8.00	4.00	4.00	0.00	0.00	0.00	-0.00	0.00
d tot	20.27	10.16	10.11	0.05	0.00	0.00	0.00	-0.00
f σ	1.97	1.00	0.98	0.02	-0.04	-0.00	-0.04	0.04
f π	4.00	2.00	2.00	-0.00	0.01	0.00	0.00	-0.00
f δ	4.00	2.00	2.00	-0.00	0.00	0.00	0.00	-0.00
f ϕ	4.00	2.00	2.00	0.00	0.00	0.00	0.00	0.00
f tot	13.97	6.99	6.98	0.02	-0.04	0.00	-0.04	0.04
Total	69.22	35.07	34.15	0.93	0.04	0.06	-0.02	0.08
F s	4.02	2.03	1.99	0.04	0.00	0.02	0.00	-0.04
p σ	1.90	0.97	0.93	0.04	-0.03	-0.03	0.01	-0.04
p π	3.85	1.92	1.93	-0.00	-0.01	-0.01	-0.01	0.00
p tot	5.75	2.89	2.86	0.04	-0.04	-0.04	-0.00	-0.03
Total	9.78	4.93	4.85	0.07	-0.04	-0.06	0.02	-0.08

TABLE S5: Summary EuF₃ Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha-\beta$	Tot	α	β	$\alpha-\beta$
Eu S	9.99	4.99	4.99	-0.00	-0.02	-0.01	-0.01	0.01
PX	7.99	4.00	3.99	0.01	-0.04	-0.02	-0.02	-0.00
PY	7.99	4.00	3.99	0.01	-0.04	-0.02	-0.02	-0.00
PZ	8.01	4.01	4.01	0.00	-0.01	-0.00	-0.00	0.00
P tot	23.99	12.00	11.99	0.01	-0.08	-0.04	-0.04	-0.00
D-2	4.22	2.12	2.10	0.02	-0.04	-0.02	-0.02	-0.00
D-1	4.13	2.07	2.06	0.01	-0.01	-0.00	-0.00	-0.00
D0	4.09	2.05	2.04	0.00	-0.00	-0.00	-0.00	-0.00
D+1	4.13	2.07	2.06	0.01	-0.01	-0.00	-0.00	-0.00
D+2	4.22	2.12	2.10	0.02	-0.04	-0.02	-0.02	-0.00
D tot	20.78	10.42	10.36	0.06	-0.10	-0.05	-0.05	-0.01
F-3	0.41	0.38	0.02	0.36	0.00	0.01	-0.00	0.01
F-2	1.01	1.00	0.01	0.99	-0.00	-0.00	-0.00	-0.00
F-1	1.01	1.00	0.01	0.99	-0.00	-0.00	-0.00	0.00
F0	0.70	0.69	0.01	0.68	-0.01	-0.01	0.00	-0.01
F+1	1.01	1.00	0.01	0.99	-0.00	-0.00	-0.00	0.00
F+2	1.01	1.00	0.01	0.99	-0.00	-0.00	-0.00	-0.00
F+3	1.03	1.01	0.02	0.99	0.01	0.00	0.00	-0.00
F tot	6.19	6.09	0.10	5.98	-0.00	-0.00	-0.00	-0.00
G tot	0.02	0.01	0.01	0.00	-0.01	-0.01	-0.01	-0.00
Total	60.97	33.52	27.46	6.06	-0.22	-0.11	-0.11	-0.00
F S	4.00	2.00	2.00	0.00	0.05	0.02	0.03	-0.00
P tot	5.66	2.82	2.84	-0.02	0.03	0.02	0.01	0.00
Total	9.68	4.83	4.85	-0.02	0.07	0.04	0.04	0.00

TABLE S6: Summary GdF₃ Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha\text{-}\beta$	Tot	α	β	$\alpha\text{-}\beta$
Gd S	10.25	5.25	5.00	0.25	-0.27	-0.25	-0.01	-0.24
PX	7.98	3.99	3.99	0.00	-0.02	-0.01	-0.01	0.00
PY	7.98	3.99	3.99	0.00	-0.02	-0.01	-0.01	0.00
PZ	8.01	4.00	4.00	-0.00	0.01	0.01	0.00	0.00
P tot	23.97	11.99	11.99	0.00	-0.04	-0.01	-0.02	0.01
D-2	4.21	2.12	2.09	0.02	-0.03	-0.02	-0.01	-0.01
D-1	4.15	2.08	2.06	0.02	-0.02	-0.02	-0.01	-0.01
D0	4.09	2.04	2.04	0.00	-0.00	0.00	-0.00	0.01
D+1	4.15	2.08	2.06	0.02	-0.02	-0.02	-0.01	-0.01
D+2	4.21	2.12	2.09	0.02	-0.03	-0.02	-0.01	-0.01
D tot	20.80	10.44	10.36	0.08	-0.12	-0.07	-0.05	-0.02
F-3	0.91	0.89	0.02	0.87	0.11	0.11	0.00	0.11
F-2	1.01	1.00	0.01	0.99	-0.00	0.00	-0.00	0.00
F-1	1.01	1.00	0.01	0.99	0.00	-0.00	0.00	-0.00
F0	0.97	0.96	0.01	0.95	0.05	0.04	0.00	0.04
F+1	1.01	1.00	0.01	0.99	0.00	-0.00	0.00	-0.00
F+2	1.01	1.00	0.01	0.99	-0.00	0.00	-0.00	0.00
F+3	1.03	1.01	0.02	0.99	0.01	0.01	0.01	-0.00
F tot	6.96	6.87	0.09	6.78	0.17	0.16	0.01	0.15
G tot	0.02	0.01	0.01	-0.00	-0.01	-0.00	-0.00	0.00
Total	61.99	34.56	27.44	7.12	-0.25	-0.18	-0.07	-0.11
F S	4.01	2.01	2.00	0.01	0.04	0.02	0.02	-0.01
P tot	5.64	2.80	2.85	-0.05	0.05	0.05	0.00	0.04
Total	9.67	4.81	4.85	-0.04	0.08	0.06	0.02	0.04

TABLE S7: Summary TbF₃ Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha-\beta$	Tot	α	β	$\alpha-\beta$
Tb S	10.56	5.00	5.57	-0.57	-0.57	0.01	-0.58	0.58
PX	8.00	4.00	4.00	0.01	-0.03	-0.02	-0.02	-0.00
PY	8.00	4.00	4.00	0.01	-0.03	-0.02	-0.02	-0.00
PZ	8.02	4.01	4.01	0.00	-0.01	-0.00	-0.01	0.00
P tot	24.02	12.02	12.00	0.01	-0.08	-0.04	-0.04	-0.01
D-2	4.23	2.12	2.11	0.01	-0.05	-0.03	-0.03	-0.00
D-1	4.13	2.07	2.06	0.01	0.00	0.00	-0.00	0.00
D0	4.12	2.05	2.07	-0.02	-0.04	-0.01	-0.03	0.02
D+1	4.13	2.07	2.06	0.01	0.00	0.00	-0.00	0.00
D+2	4.23	2.12	2.11	0.01	-0.05	-0.03	-0.03	-0.00
D tot	20.83	10.43	10.40	0.03	-0.14	-0.06	-0.08	0.02
F-3	1.26	1.00	0.25	0.75	0.04	-0.00	0.05	-0.05
F-2	1.01	1.00	0.01	0.99	0.00	-0.00	0.00	-0.00
F-1	1.02	1.00	0.01	0.99	-0.00	-0.00	-0.00	0.00
F0	1.13	1.00	0.12	0.88	0.60	0.00	0.60	-0.60
F+1	1.02	1.00	0.01	0.99	-0.00	-0.00	-0.00	0.00
F+2	1.01	1.00	0.01	0.99	0.00	-0.00	0.00	-0.00
F+3	1.03	1.01	0.02	0.98	0.01	0.00	0.01	-0.00
F tot	7.48	7.03	0.45	6.58	0.65	-0.00	0.65	-0.66
G tot	0.02	0.01	0.01	-0.00	-0.01	-0.00	-0.00	0.00
Total	62.91	34.48	28.43	6.05	-0.14	-0.10	-0.04	-0.06
F S	4.01	2.00	2.01	-0.01	0.03	0.02	0.01	0.01
P tot	5.66	2.83	2.83	-0.00	0.02	0.01	0.01	0.01
Total	9.70	4.84	4.86	-0.02	0.05	0.03	0.01	0.02

TABLE S8: Summary YbF₃ Mulliken populations

	ECP(seg)				AE-ECP(seg)			
	Tot	α	β	$\alpha-\beta$	Tot	α	β	$\alpha-\beta$
Yb S	10.01	5.01	5.00	0.00	0.02	0.01	0.01	0.00
PX	8.02	4.01	4.01	-0.00	-0.03	-0.01	-0.01	0.00
PY	8.02	4.01	4.01	-0.00	-0.03	-0.01	-0.01	0.00
PZ	8.03	4.02	4.01	0.00	-0.00	-0.00	-0.00	-0.00
P tot	24.07	12.03	12.03	-0.00	-0.06	-0.03	-0.03	-0.00
D-2	4.23	2.12	2.11	0.00	-0.05	-0.03	-0.02	-0.00
D-1	4.11	2.06	2.06	0.00	0.01	0.00	0.00	-0.00
D0	4.07	2.04	2.03	0.00	0.01	0.00	0.00	0.00
D+1	4.11	2.06	2.06	0.00	0.01	0.00	0.00	-0.00
D+2	4.23	2.12	2.11	0.00	-0.05	-0.03	-0.02	-0.00
D tot	20.75	10.38	10.37	0.01	-0.08	-0.04	-0.04	-0.00
F-3	1.40	1.00	0.39	0.61	0.00	-0.00	0.00	-0.00
F-2	2.00	1.00	1.00	0.00	0.00	0.00	0.00	-0.00
F-1	2.01	1.00	1.00	0.00	-0.00	-0.00	-0.00	-0.00
F0	1.64	1.00	0.64	0.36	0.00	0.00	0.00	-0.00
F+1	2.01	1.00	1.00	0.00	-0.00	-0.00	-0.00	-0.00
F+2	2.00	1.00	1.00	0.00	0.00	0.00	0.00	-0.00
F+3	2.02	1.01	1.01	0.00	0.01	0.00	0.00	-0.00
F tot	13.08	7.03	6.05	0.97	0.01	0.00	0.01	-0.00
G tot	0.02	0.01	0.01	-0.00	0.00	0.00	0.00	0.00
Total	67.94	34.46	33.48	0.98	-0.10	-0.05	-0.05	-0.00
F S	4.00	2.00	2.00	0.00	0.03	0.01	0.01	0.00
P tot	5.67	2.84	2.83	0.00	0.01	0.00	0.00	0.00
Total	9.69	4.85	4.84	0.01	0.03	0.02	0.02	0.00

TABLE S9: Summary spin-orbit splitting, in cm^{-1} .

Gd					
$^9D^o(7, 1, 2)$			$^{11}F(7, 2, 1)$		
m_j	Exp	Calc	m_j	Exp	Calc ^b
2.0	0.0	0.0	2.0	6378.1	6378.1
3.0	215.1	359.2	3.0	6550.4	6612.3
4.0	533.0	838.2	4.0	6786.2	6924.6
5.0	999.1	1436.9	5.0	7103.4	7314.9
6.0	1719.1	2155.3	6.0	7480.3	7783.3
			7.0	7947.3	8329.8
			8.0	8498.4	8954.3
Avg	1197.4	880.9		7783.3	7505.0
Δ				6585.9	6624.1
Tb					
$^6H^o(9, 0, 2)$			$^8G(8, 1, 2)$		
7.5	0.0	0.0	6.5	285.5	285.5
6.5	2771.7	2746.4	7.5	462.1	-611.4
5.5	4670.4	5127.2	5.5	509.9	1062.8
4.5	6174.9	7141.7	3.5	2419.5	2260.1
3.5	8789.8 ^c	8789.8	4.5	2840.2	1721.5
2.5	10072.1 ^c	10072.1	2.5	3174.6	2679.4
			1.5	3705.8	2978.9
			0.5	4018.2	3158.9
Avg	4577.9	4353.8		1063.6	1488.5
Δ				-3514.4	-2865.2

^a The state is followed by the number of 4f, 5d, and 6s electrons.

^b Lowest m_j level shifted to agree with experiment.

^c Experimental level is missing, theory is used instead.

TABLE S10: Summary spin-orbit splitting, in cm^{-1} .

Dy					
$^5I(10, 0, 2)$			$^7H^o(9, 1, 2)$		
m_j	Exp	Calc	m_j	Exp	Calc ^b
8.0	0.0	0.0	8.0	7565.6	7565.6
7.0	4134.2	3911.8	7.0	8519.2	9771.9
6.0	7050.6	7335.3	6.0	10088.8	11703.5
5.0	9211.6	10268.6	5.0	12298.6	13359.2
4.0	10925.3	12713.4	4.0	13952.0	14738.9
			3.0	15254.9	15842.2
			2.0	16669.7 ^c	16669.7
Avg	5867.9	5435.8		11703.7	10890.2
Δ				5835.9	5454.4

^a The state is followed by the number of 4f, 5d, and 6s electrons.

^b Lowest m_j level shifted to agree with experiment.

^c Experimental level is missing, theory is used instead.

TABLE S11: Summary Er spin-orbit splitting, in cm^{-1} .

$^3H(12,0,2)$ ground state							
m_j	theory	expt					
6	0	0.0					
5	6910	6958.3					
4	12672	10751.0					
m_j	excite states (11,1,2)						expt
	$^5G^o$	$+^5H^o$	$+^5L^o$	$+^5K^o$	$+^5I^0$	+triplets	$(\frac{15}{2}, \frac{3}{2})^o$ $(\frac{15}{2}, \frac{5}{2})^o$
6.0	0	0	0	0	0	0	0.0
7.0		1671	1671	1671	911	885	520.5
9.0			6561	3038	3108	1743	1444.1
8.0			10128	6825	3186	2650	2173.6
10.0			2598	2598	2668	2966	2479.3
9.0				7402	7472	4525	3381.4
5.0	5813	5419	5419	5419	5369	5106	4224.7
8.0				11321	7850	5760	4381.2
6.0		7332	7332	7332	6230	5861	4623.3
7.0			13299	10471	7792	6481	4711.0
8.0					11598	7971	
7.0				14524	11927	9700	
9.0						9802	
5.0		11928	11928	11928	10892	10011	
4.0	10657	10195	10195	10195	10163	10188	
6.0			16073	13961	11965	10925	

TABLE S12: Summary Tm spin-orbit splitting, in cm^{-1} .

$^2F^o(13,0,2)$ ground state									
m_j	theory	expt							
7/2	0	0.0							
5/2	8855	8771.2							
m_j	excite states (11,1,2)						expt		
	4F	4K	4G	4H	4I	+doublets	$(6, \frac{3}{2})$	$(6, \frac{5}{2})$	
9/2	0	0	0	0	0	0	0.0		
15/2		7471	8268	8311	5879	2523	2151.4		
11/2		14983	4134	3296	3247	3339	2468.2		
17/2		2910	3707	3751	3751	3975	3337.3		
7/2	6610	6610	6380	6375	6375	5303	3837.4		
13/2		11495	12292	7800	6558	5692	4335.2		
15/2					10043	7496	5573.5		
11/2			15780	13289	11712	8099	5734.2		
9/2			10451	9342	9282	8152	5717.8		
13/2				12336	10897	8398	6347.1		
13/2					14997	10730			

TABLE S13: Summary Yb spin-orbit splitting, in cm^{-1} .

$^1S(14,0,2)$ ground state

m_j theory expt

0 0 0.0

m_j	excite states (13,1,2)						expt
	$^3P^o$	$+^3H^o$	$+^3D^o$	$+^3F^o$	$+^3G^0$	+singlets	$(\frac{7}{2}, \frac{3}{2})^o$ $(\frac{7}{2}, \frac{5}{2})^o$
2.0	0	0	0	0	0	0	0.0
5.0		7652	8897	8961	7146	3104	2671.2
6.0		3659	4903	4967	4967	4967	4126.4
3.0			7420	5480	5318	5144	4257.1
1.0	7007	7007	7176	7240	7240	6272	5668.5
4.0		10987	12232	8629	6953	6423	4996.0
2.0			13097	11121	11120	6554	5007.4
4.0				12295	11536	8784	6586.4
3.0				14511	13071	9080	7018.9
5.0					12215	9594	7336.2
0							