

## Supporting Information

# Understanding Single Molecule Magnet Properties of Lanthanide Complexes by 4f Orbital Splitting

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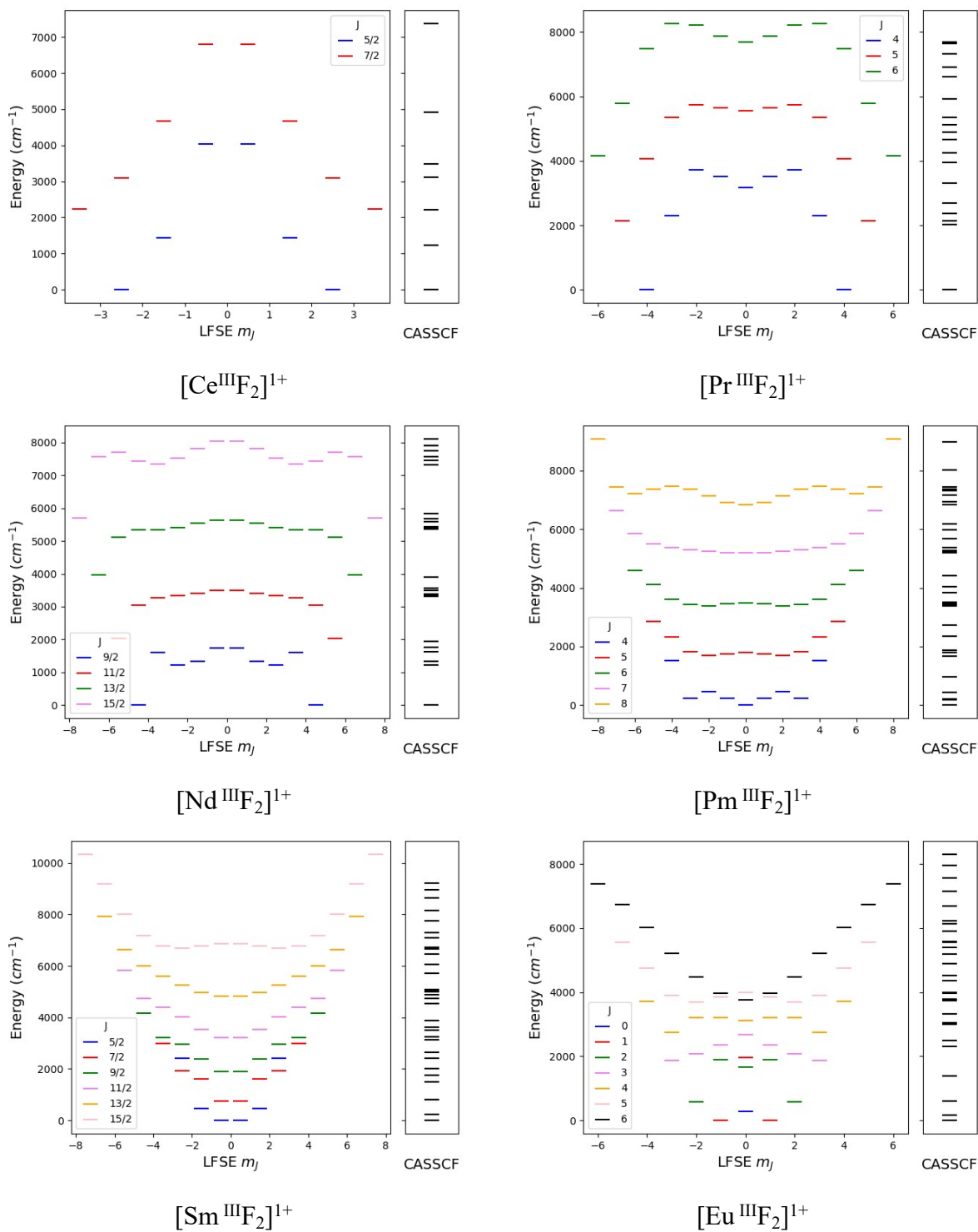
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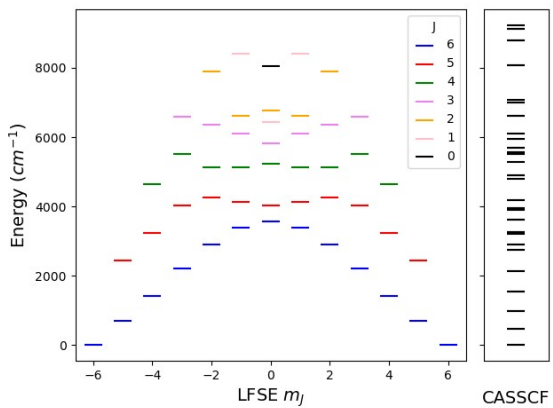
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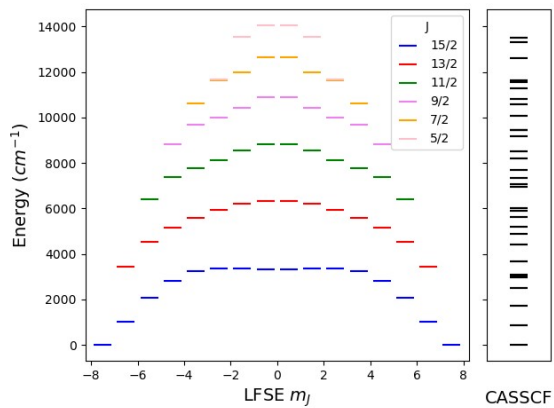
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**Figure S1.** Energy splitting of the  $[\text{Ln}^{\text{III}}\text{F}_2]^{1+}$  models calculated by the Ligand Field Stabilization Energy (LFSE) model and CASSCF(n,7).

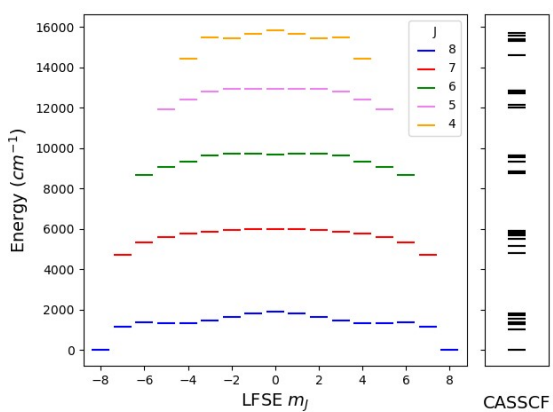




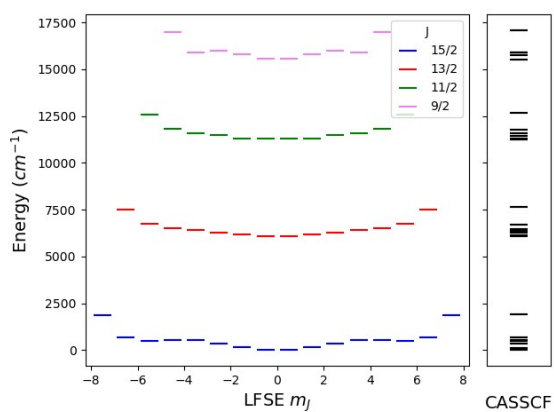
[Tb III F<sub>2</sub>]<sup>1+</sup>



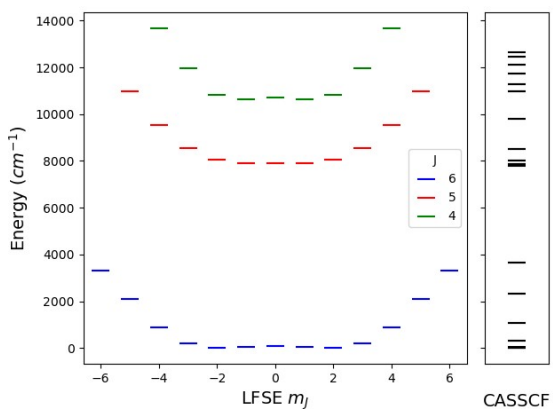
[Dy III F<sub>2</sub>]<sup>1+</sup>



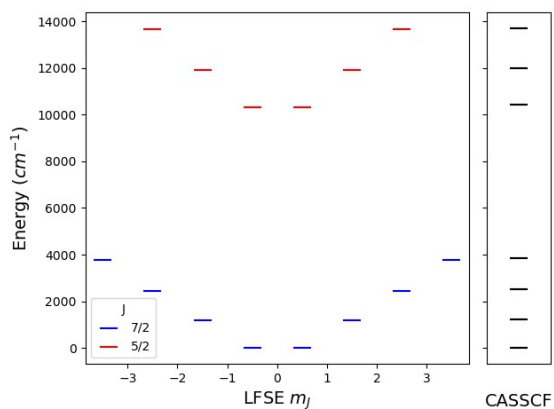
[Ho III F<sub>2</sub>]<sup>1+</sup>



[Er III F<sub>2</sub>]<sup>1+</sup>



[Tm III F<sub>2</sub>]<sup>1+</sup>



[Yb III F<sub>2</sub>]<sup>1+</sup>

**Table S1.** f-Orbital contributions for the ground term of Ce<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Ce <sup>III</sup>	5/2	±5/2	0.86	0.14	0.00	0.00
		±3/2	0.00	0.71	0.29	0.00
		±1/2	0.00	0.00	0.57	0.43
	7/2	±7/2	1.00	0.00	0.00	0.00
		±5/2	0.14	0.86	0.00	0.00
		±3/2	0.00	0.29	0.71	0.00
		±1/2	0.00	0.00	0.43	0.57

**Table S2.** f-Orbital contributions for the ground term of Pr<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Pr <sup>III</sup>	4	±4	0.99	0.82	0.17	0.01
		±3	0.87	0.13	0.77	0.23
		±2	0.48	0.51	0.39	0.62
		±1	0.19	0.73	0.73	0.36
		0	0.09	0.76	1.02	0.13
	5	±5	1.00	0.83	0.17	0.00
		±4	0.90	0.27	0.63	0.20
		±3	0.63	0.37	0.53	0.47
		±2	0.37	0.58	0.59	0.47
		±1	0.18	0.72	0.78	0.32
	6	0	0.12	0.76	0.88	0.24
		±6	1.00	1.00	0.00	0.00
		±5	1.00	0.17	0.83	0.00
		±4	0.77	0.24	0.53	0.45
		±3	0.50	0.50	0.36	0.64
		±2	0.27	0.68	0.57	0.48
		±1	0.13	0.75	0.90	0.23
		0	0.08	0.76	1.05	0.11

**Table S3.** f-Orbital contributions for the ground term of Nd<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Nd <sup>III</sup>	9/2	±9/2	1.00	0.98	0.81	0.21
		±7/2	0.99	0.80	0.48	0.73
		±5/2	0.91	0.57	1.23	0.29
		±3/2	0.76	0.80	1.12	0.32
		±1/2	0.63	1.13	0.65	0.59
	11/2	±11/2	1.00	0.99	0.76	0.26
		±9/2	0.99	0.79	0.70	0.52
		±7/2	0.93	0.69	0.92	0.46
		±5/2	0.83	0.76	1.00	0.41
		±3/2	0.73	0.90	0.93	0.44
	13/2	±1/2	0.67	1.01	0.84	0.48
		±13/2	1.00	1.00	0.80	0.20
		±11/2	1.00	0.85	0.58	0.57
		±9/2	0.96	0.69	0.85	0.49
		±7/2	0.88	0.68	1.05	0.39
	15/2	±5/2	0.79	0.79	1.03	0.38
		±3/2	0.71	0.94	0.90	0.45
		±1/2	0.66	1.05	0.78	0.51
		±15/2	1.00	1.00	1.00	0.00
		±13/2	1.00	1.00	0.20	0.80
		±11/2	1.00	0.71	0.66	0.63
		±9/2	0.96	0.54	1.18	0.32
		±7/2	0.87	0.58	1.34	0.21
	±5/2	0.76	0.79	1.14	0.31	
	±3/2	0.66	1.04	0.79	0.51	
	±1/2	0.61	1.20	0.54	0.65	

**Table S4.** f-Orbital contributions for the ground term of Pm<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals				
			±3	±2	±1	0	
Pm <sup>III</sup>	4	±4	1.00	1.03	1.22	0.74	
		±3	1.03	1.24	1.37	0.36	
		±2	1.14	1.36	0.80	0.70	
		±1	1.29	1.07	1.07	0.57	
		0	1.37	0.87	1.35	0.41	
	5	±5	1.00	1.04	1.30	0.66	
		±4	1.03	1.27	1.07	0.63	
		±3	1.12	1.20	1.19	0.49	
		±2	1.21	1.13	1.17	0.48	
		±1	1.27	1.10	1.06	0.57	
		0	1.29	1.09	1.00	0.62	
	6	±6	1.00	1.03	1.31	0.66	
		±5	1.01	1.25	1.08	0.65	
		±4	1.08	1.23	1.15	0.52	
		±3	1.17	1.16	1.20	0.47	
		±2	1.24	1.11	1.14	0.51	
		±1	1.28	1.09	1.05	0.58	
		0	1.29	1.09	1.00	0.61	
		7	±7	1.00	1.00	1.25	0.75
	±6		1.00	1.18	1.29	0.54	
	±5		1.04	1.27	1.16	0.52	
	±4		1.11	1.27	1.07	0.55	
	±3		1.19	1.20	1.04	0.57	
	±2		1.26	1.11	1.07	0.56	
	±1		1.31	1.03	1.12	0.54	
	0		1.33	1.00	1.14	0.53	
	8		±8	1.00	1.00	1.00	1.00
			±7	1.00	1.00	1.75	0.25
			±6	1.00	1.25	1.40	0.35
		±5	1.04	1.43	0.91	0.62	
		±4	1.11	1.43	0.70	0.76	
		±3	1.21	1.27	0.80	0.72	
±2		1.30	1.06	1.08	0.57		
±1		1.37	0.87	1.35	0.41		
0		1.39	0.80	1.46	0.35		

**Table S5.** f-Orbital contributions for the ground term of Sm<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>J</sub>	Orbitals			
			±3	±2	±1	0
Sm <sup>III</sup>	5/2	±5/2	1.08	1.37	1.65	0.88
		±3/2	1.43	1.60	1.36	0.61
		±1/2	1.77	1.32	1.27	0.64
	7/2	±7/2	1.10	1.47	1.58	0.85
		±5/2	1.42	1.30	1.63	0.65
		±3/2	1.55	1.54	1.05	0.87
		±1/2	1.64	1.40	1.45	0.49
		±9/2	1.08	1.50	1.55	0.86
	9/2	±7/2	1.36	1.28	1.73	0.63
		±5/2	1.49	1.47	1.20	0.85
		±3/2	1.57	1.48	1.20	0.72
		±1/2	1.63	1.41	1.46	0.50
		±11/2	1.04	1.47	1.57	0.93
		±9/2	1.27	1.32	1.79	0.62
		±7/2	1.42	1.46	1.34	0.78
	11/2	±5/2	1.53	1.51	1.15	0.80
		±3/2	1.63	1.44	1.27	0.65
		±1/2	1.68	1.37	1.45	0.51
		±13/2	1.00	1.33	1.67	1.00
		±11/2	1.15	1.44	1.72	0.69
		±9/2	1.31	1.54	1.46	0.69
		±7/2	1.46	1.55	1.27	0.72
	13/2	±5/2	1.60	1.47	1.23	0.69
		±3/2	1.71	1.37	1.29	0.63
		±1/2	1.77	1.30	1.36	0.58
		±15/2	1.00	1.00	2.00	1.00
		±13/2	1.00	1.67	1.33	1.00
		±11/2	1.14	1.76	1.38	0.71
±9/2		1.34	1.64	1.53	0.49	
15/2	±7/2	1.54	1.48	1.53	0.45	
	±5/2	1.70	1.35	1.39	0.55	
	±3/2	1.82	1.28	1.20	0.70	
	±1/2	1.88	1.25	1.06	0.80	

**Table S6.** f-Orbital contributions for the ground term of Eu<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Eu <sup>III</sup>	0	0	1.71	1.71	1.71	0.86
		1	±1	1.89	1.71	1.61
	1	0	1.36	1.71	1.93	1.00
		±2	1.88	1.76	1.60	0.76
		±1	1.70	1.52	1.80	0.98
	2	0	1.40	2.00	1.79	0.81
		±3	1.83	1.67	1.67	0.83
		±2	1.67	1.83	1.67	0.83
		±1	1.67	1.67	1.83	0.83
	3	0	1.67	1.67	1.67	1.00
		±4	1.73	1.55	1.73	1.00
		±3	1.59	1.91	1.91	0.59
		±2	1.65	1.98	1.39	0.98
		±1	1.81	1.60	1.69	0.90
	4	0	1.88	1.36	1.99	0.77
		±5	1.50	1.50	2.00	1.00
		±4	1.50	2.00	1.50	1.00
		±3	1.67	1.83	1.83	0.67
		±2	1.83	1.67	1.83	0.67
		±1	1.94	1.62	1.56	0.88
	5	0	1.98	1.62	1.40	1.00
		±6	1.00	2.00	2.00	1.00
		±5	1.50	1.50	2.00	1.00
		±4	1.77	1.45	1.77	1.00
		±3	1.91	1.59	1.59	0.91
		±2	1.97	1.76	1.52	0.76
		±1	1.99	1.88	1.51	0.62
		0	2.00	1.92	1.51	0.57



**Table S7.** f-Orbital contributions for the ground term of Tb<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Tb <sup>III</sup>	6	±6	3.00	2.00	2.00	1.00
		±5	2.50	2.50	2.00	1.00
		±4	2.23	2.55	2.23	1.00
		±3	2.09	2.41	2.41	1.09
		±2	2.03	2.24	2.48	1.24
		±1	2.01	2.12	2.49	1.38
		0	2.00	2.08	2.49	1.43
	5	±5	2.50	2.50	2.00	1.00
		±4	2.50	2.00	2.50	1.00
		±3	2.33	2.17	2.17	1.33
		±2	2.17	2.33	2.17	1.33
		±1	2.06	2.38	2.44	1.12
		0	2.02	2.38	2.60	1.00
		4	±4	2.27	2.45	2.27
	±3		2.41	2.09	2.09	1.41
	±2		2.35	2.02	2.61	1.02
	±1		2.19	2.40	2.31	1.10
	0		2.12	2.64	2.01	1.23
	3	±3	2.17	2.33	2.33	1.17
		±2	2.33	2.17	2.33	1.17
		±1	2.33	2.33	2.17	1.17
		0	2.33	2.33	2.33	1.00
	2	±2	2.12	2.24	2.40	1.24
		±1	2.30	2.48	2.20	1.02
		0	2.60	2.00	2.21	1.19
	1	±1	2.11	2.29	2.39	1.21
		0	2.64	2.29	2.07	1.00
	0	0	2.29	2.29	2.29	1.14

**Table S8.** f-Orbital contributions for the ground term of Dy<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals				
			±3	±2	±1	0	
Dy <sup>III</sup>	15/2	±15/2	3.00	3.00	2.00	1.00	
		±13/2	3.00	2.33	2.67	1.00	
		±11/2	2.86	2.24	2.62	1.29	
		±9/2	2.66	2.36	2.47	1.51	
		±7/2	2.46	2.52	2.47	1.55	
		±5/2	2.29	2.65	2.61	1.45	
		±3/2	2.18	2.72	2.80	1.30	
		±1/2	2.12	2.75	2.94	1.20	
	13/2	±13/2	3.00	2.67	2.33	1.00	
		±11/2	2.85	2.56	2.28	1.31	
		±9/2	2.69	2.46	2.54	1.31	
		±7/2	2.54	2.45	2.73	1.28	
		±5/2	2.40	2.53	2.77	1.31	
		±3/2	2.29	2.63	2.71	1.37	
		±1/2	2.23	2.70	2.64	1.42	
		11/2	±11/2	2.96	2.53	2.43	1.07
	±9/2		2.73	2.68	2.21	1.38	
	±7/2		2.58	2.54	2.66	1.22	
	±5/2		2.47	2.49	2.85	1.20	
	±3/2		2.37	2.55	2.72	1.34	
	±1/2		2.32	2.63	2.55	1.49	
	9/2		±9/2	2.92	2.50	2.45	1.14
			±7/2	2.64	2.72	2.27	1.37
		±5/2	2.51	2.53	2.80	1.15	
		±3/2	2.41	2.50	2.78	1.27	
		±1/2	2.36	2.59	2.54	1.50	
	7/2	±7/2	2.90	2.53	2.42	1.15	
		±5/2	2.58	2.70	2.37	1.35	
±3/2		2.45	2.46	2.95	1.13		
±1/2		2.35	2.59	2.53	1.50		
5/2		±5/2	2.91	2.62	2.34	1.11	
	±3/2	2.57	2.40	2.64	1.39		
	±1/2	2.23	2.68	2.73	1.36		

**Table S9.** f-Orbital contributions for the ground term of Ho<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Ho <sup>III</sup>	8	±8	3.00	3.00	3.00	1.00
		±7	3.00	3.00	2.25	1.75
		±6	3.00	2.75	2.60	1.65
		±5	2.96	2.57	3.09	1.38
		±4	2.89	2.57	3.30	1.23
		±3	2.79	2.73	3.20	1.28
		±2	2.70	2.94	2.92	1.43
		±1	2.63	3.13	2.65	1.59
	7	0	2.61	3.20	2.54	1.65
		±7	3.00	3.00	2.75	1.25
		±6	3.00	2.82	2.71	1.46
		±5	2.96	2.73	2.84	1.48
		±4	2.89	2.73	2.93	1.45
		±3	2.81	2.80	2.96	1.43
		±2	2.74	2.89	2.93	1.44
		±1	2.69	2.97	2.88	1.46
	6	0	2.67	3.00	2.86	1.47
		±6	3.00	2.97	2.69	1.34
		±5	2.99	2.75	2.92	1.35
		±4	2.90	2.75	2.83	1.47
		±3	2.83	2.84	2.80	1.53
		±2	2.76	2.89	2.86	1.49
		±1	2.72	2.91	2.95	1.42
		0	2.71	2.91	3.00	1.39
	5	±5	3.00	2.96	2.70	1.34
		±4	2.97	2.73	2.93	1.37
		±3	2.88	2.80	2.81	1.51
		±2	2.78	2.87	2.82	1.51
		±1	2.73	2.90	2.94	1.43
		0	2.71	2.91	3.00	1.38
	4	±4	2.99	2.96	2.77	1.26
		±3	2.97	2.76	2.63	1.64
±2		2.86	2.64	3.20	1.30	
±1		2.71	2.93	2.93	1.43	
0		2.63	3.13	2.65	1.59	

**Table S10.** f-Orbital contributions for the ground term of Er<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals				
			±3	±2	±1	0	
Er <sup>III</sup>	15/2	±15/2	3.00	3.00	3.00	2.00	
		±13/2	3.00	3.00	3.80	1.20	
		±11/2	3.00	3.29	3.34	1.37	
		±9/2	3.04	3.46	2.82	1.68	
		±7/2	3.13	3.42	2.66	1.79	
		±5/2	3.24	3.21	2.86	1.69	
		±3/2	3.34	2.96	3.21	1.49	
		±1/2	3.39	2.80	3.46	1.35	
	13/2	±13/2	3.00	3.00	3.20	1.80	
		±11/2	3.00	3.15	3.42	1.43	
		±9/2	3.04	3.31	3.15	1.51	
		±7/2	3.12	3.32	2.95	1.61	
		±5/2	3.21	3.21	2.97	1.62	
		±3/2	3.29	3.06	3.10	1.55	
		±1/2	3.34	2.95	3.22	1.49	
		11/2	±11/2	3.00	3.01	3.24	1.74
	±9/2		3.01	3.21	3.30	1.48	
	±7/2		3.07	3.31	3.08	1.54	
	±5/2		3.17	3.24	3.00	1.59	
	±3/2		3.26	3.09	3.06	1.56	
	±1/2		3.33	2.99	3.16	1.52	
	9/2		±9/2	3.00	3.02	3.19	1.79
			±7/2	3.01	3.20	3.52	1.27
		±5/2	3.09	3.43	2.77	1.71	
		±3/2	3.24	3.20	2.88	1.68	
		±1/2	3.37	2.87	3.35	1.41	

**Table S11.** f-Orbital contributions for the ground term of Tm<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Tm <sup>III</sup>	6	±6	3.00	3.00	4.00	2.00
		±5	3.00	3.83	3.17	2.00
		±4	3.23	3.76	3.47	1.55
		±3	3.50	3.50	3.64	1.36
		±2	3.73	3.32	3.43	1.52
		±1	3.87	3.25	3.10	1.77
		0	3.92	3.24	2.95	1.89
	5	±5	3.00	3.17	3.83	2.00
		±4	3.10	3.73	3.37	1.80
		±3	3.37	3.63	3.47	1.53
		±2	3.63	3.42	3.41	1.53
		±1	3.82	3.28	3.22	1.68
		0	3.88	3.24	3.12	1.76
	4	±4	3.01	3.18	3.83	1.99
		±3	3.13	3.87	3.23	1.77
		±2	3.52	3.49	3.61	1.38
		±1	3.81	3.27	3.27	1.64
		0	3.91	3.24	2.98	1.87

**Table S12.** f-Orbital contributions for the ground term of Yb<sup>III</sup>

Ln <sup>III</sup>	J	m <sub>j</sub>	Orbitals			
			±3	±2	±1	0
Yb <sup>III</sup>	7/2	±7/2	3.00	4.00	4.00	2.00
		±5/2	3.86	3.14	4.00	2.00
		±3/2	4.00	3.71	3.29	2.00
		±1/2	4.00	4.00	3.57	1.43
	5/2	±5/2	3.14	3.86	4.00	2.00
		±3/2	4.00	3.29	3.71	2.00
		±1/2	4.00	4.00	3.43	1.57

