Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Study of the Most Relevant Spin-Orbit Coupling Descriptions of Magnetic Excitations in a Series of Lanthanide Complexes

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Table S1: Mean μ and standard deviation σ for the %errors affecting the energy gaps within the lowest energy spin-orbit multiplets for Ln-acac$_3$-(H$_2$O)$_2$ complexes, estimated using different approximations to spin-orbit coupling Hamiltonian with respect to the results obtained by inclusion of the true Breit-Pauli Hamiltonian contribution. Between parenthesis the mean absolute errors (MAE) when different from $|\mu|$. Computations at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C, [2s] for H.

			$\mathcal{H}_{\rm SO}^{(1)}$	$\mathcal{H}_{\rm SO}^{\rm MF}$	$\mathcal{H}_{\rm SO}^{\rm AMF}$	$\mathcal{H}_{\rm SO}^{\rm ABP}$
Pr(III)	^{3}H$_4$	μ	−5.396	0.110	0.192	0.082
		σ	3.888	0.179	0.055	0.132
			–	–	–	(0.141)
	^{3}H$_5$	μ	110.704	0.286	0.292	0.006
		σ	8.275	0.021	0.027	0.007
			–	–	–	(0.008)
Nd(III)	^{4}I$_{9/2}$	μ	−6.263	0.009	0.307	0.310
		σ	1.757	0.012	0.103	0.100
			–	(0.012)	–	–
	^{4}I$_{11/2}$	μ	122.487	1.355	1.367	0.013
		σ	4.852	0.054	0.057	0.003
			–	–	–	–
Sm(III)	^{6}H$_{5/2}$	μ	−1.143	−0.173	−0.394	−0.225
		σ	1.629	0.171	0.202	0.032
			(1.152)	–	–	–
	^{6}H$_{7/2}$	μ	139.270	3.311	3.269	−0.043
		σ	14.078	0.352	0.347	0.006
			–	–	–	–
Eu(III)	^{7}F$_1$	μ	332.099	3.597	3.596	−0.002
		σ	138.924	1.496	1.562	0.067
			–	–	–	(0.048)
	^{7}F$_2$	μ	241.787	3.614	3.603	−0.012
		σ	23.919	0.357	0.379	0.022
			–	–	–	(0.020)
	^{7}F$_3$	μ	199.905	3.969	3.959	−0.011
		σ	4.856	0.110	0.121	0.016
			–	–	–	(0.017)
	^{7}F$_4$	μ	171.805	4.402	4.393	−0.009
		σ	5.272	0.141	0.138	0.006
			–	–	–	(0.010)
	^{7}F$_5$	μ	150.097	4.874	4.867	−0.008
		σ	4.334	0.153	0.143	0.011
			–	–	–	(0.009)
	^{7}F$_6$	μ	131.530	5.381	5.375	−0.007
		σ	4.176	0.157	0.146	0.014
			–	–	–	(0.013)

Gd(III)	$^{8}H_{7/2}$	μ	348.856	0.023	−11.697	−11.716
		σ	17.186	0.020	5.138	5.119
			–	–	–	–
	$^{6}P_{7/2}$	μ	−7.932	0.033	0.033	0.000
		σ	0.101	0.000	0.000	0.000
			–	–	–	–
Tb(III)	$^{7}F_{6}$	μ	−0.063	−0.305	−0.076	0.227
		σ	2.040	0.200	0.449	0.299
			(1.693)	–	(0.205)	(0.339)
	$^{7}F_{5}$	μ	97.419	−3.595	−3.573	0.024
		σ	5.425	0.193	0.201	0.009
			–	–	–	–
Dy(III)	$^{6}H_{15/2}$	μ	−3.570	−0.095	0.111	0.211
		σ	0.881	0.043	0.081	0.069
			–	–	–	–
	$^{6}H_{13/2}$	μ	99.011	−2.967	−2.958	0.011
		σ	3.176	0.093	0.102	0.010
			–	–	–	(0.012)
Ho(III)	$^{5}I_{8}$	μ	−10.770	−0.196	0.343	0.562
		σ	0.668	0.055	0.749	0.726
			–	–	(0.627)	(0.807)
	$^{5}I_{7}$	μ	97.141	−2.207	−2.195	0.013
		σ	1.063	0.022	0.033	0.012
			–	–	–	(0.014)
Er(III)	$^{4}I_{15/2}$	μ	1.180	−0.047	−0.971	−0.923
		σ	1.655	0.038	1.034	1.038
			(1.695)	–	–	–
	$^{4}I_{13/2}$	μ	89.393	−1.194	−1.213	−0.018
		σ	0.996	0.014	0.010	0.007
			–	–	–	–
Tm(III)	$^{3}H_{6}$	μ	−0.021	−0.020	−0.484	−0.460
		σ	0.665	0.015	0.512	0.516
			(0.529)	–	(0.667)	(0.649)
	$^{3}H_{5}$	μ	9.628	−0.734	−0.757	−0.022
		σ	37.226	0.179	0.180	0.002
			(21.252)	–	–	–
Yb(III)	$^{2}F_{7/2}$	μ	0.703	0.004	−0.267	−0.267
		σ	0.258	0.001	0.108	0.108
			–	–	–	–
	$^{2}F_{5/2}$	μ	79.167	0.258	0.247	−0.011
		σ	1.090	0.004	0.001	0.004
			–	–	–	–

Table S2: Mean μ and standard deviation σ for the %errors affecting the energy gaps within the ground $^6H_{15/2}$ and first excited $^6H_{13/2}$ spin-orbit multiplet for different Dy(III) complexes, estimated using different approximations to spin-orbit coupling Hamiltonian with respect to the results obtained by inclusion of the true Breit-Pauli Hamiltonian contribution. Between parenthesis the mean absolute errors (MAE) when different from $|\mu|$. Computations at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for N and O when coordinating the metal, [3s2p] for N and O not coordinating the metal, C, F, S, and [2s] for H.

			$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$
$acac_3$-$(H_2O)_2$	$^6H_{15/2}$	μ	−3.570	−0.095	0.111	0.211
		σ	0.881	0.043	0.081	0.069
			–	–	–	–
	$^6H_{13/2}$	μ	99.011	−2.967	−2.958	0.011
		σ	3.176	0.093	0.102	0.010
			–	–	–	(0.012)
$acac_3$-dppz	$^6H_{15/2}$	μ	−3.800	−0.096	−0.015	0.088
		σ	1.095	0.044	0.074	0.075
			–	–	(0.051)	(0.108)
	$^6H_{13/2}$	μ	99.662	−2.984	−2.985	0.000
		σ	2.733	0.080	0.084	0.006
			–	–	–	(0.004)
$acac_3$-dpq	$^6H_{15/2}$	μ	−3.777	−0.096	−0.091	0.011
		σ	0.964	0.036	0.069	0.053
			–	–	(0.103)	(0.039)
	$^6H_{13/2}$	μ	100.161	−2.999	−3.004	−0.004
		σ	3.052	0.089	0.091	0.004
			–	–	–	(0.005)
$acac_3$-phen	$^6H_{15/2}$	μ	−3.899	−0.097	−0.014	0.091
		σ	1.141	0.041	0.107	0.109
			–	–	(0.081)	(0.120)
	$^6H_{13/2}$	μ	99.780	−2.988	−2.988	0.001
		σ	3.025	0.088	0.096	0.010
			–	–	–	(0.007)
$hfac_3$-glyme	$^6H_{15/2}$	μ	−3.330	−0.086	0.097	0.189
		σ	1.267	0.030	0.149	0.144
			–	–	(0.138)	(0.206)
	$^6H_{13/2}$	μ	101.368	−3.032	−3.027	0.006
		σ	2.422	0.071	0.086	0.017
			–	–	–	(0.013)
trensal	$^6H_{15/2}$	μ	1.396	−0.127	−0.026	0.107
		σ	5.883	0.061	0.074	0.043
			(4.962)	–	(0.046)	–
	$^6H_{13/2}$	μ	99.872	−2.989	−2.988	0.001
		σ	4.005	0.114	0.120	0.007
			–	–	–	(0.006)

$paah_2$-$2no_3$-meoh	$^6H_{15/2}$	μ	−3.227	−0.088	0.096	0.197
		σ	2.059	0.017	0.078	0.066
			–	–	–	–
	$^6H_{13/2}$	μ	100.177	−2.999	−2.993	0.007
		σ	2.953	0.085	0.092	0.008
			–	–	–	(0.008)
tta_3-phen	$^6H_{15/2}$	μ	−3.336	−0.098	0.119	0.229
		σ	1.314	0.035	0.058	0.044
			–	–	–	–
	$^6H_{13/2}$	μ	100.652	−3.012	−3.005	0.008
		σ	2.833	0.082	0.093	0.011
			–	–	–	(0.010)
tta_3-bipy	$^6H_{15/2}$	μ	−3.936	−0.099	0.059	0.167
		σ	0.847	0.029	0.161	0.156
			–	–	(0.119)	(0.178)
	$^6H_{13/2}$	μ	100.880	−3.019	−3.014	0.006
		σ	2.441	0.071	0.088	0.019
			–	–	–	(0.016)

Table S3: Lowest energy levels in cm^{-1} for Eu^{3+} atom, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h]. Experimental values from: W.C. Martin, R.Zalubas, and L. Hagan, *Atomic energy levels - the rare-earth elements*, Tech. Rep. (National Bureau of Standards, Gaithersburg, MD, 1978).

		$\mathcal{H}_{\mathrm{SO}}^{(1)}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{MF}}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{BP}}$	EXP.
1	$^7F_0$	0	0	0	0
2	$^7F_1$	1529	382	369	370
3	$^7F_2$	3582	1067	1028	1040
4	$^7F_3$	5765	1967	1889	1890
5	$^7F_4$	7922	3010	2880	2860
6	$^7F_5$	9968	4145	3949	3910
7	$^7F_6$	11813	5334	5056	4940

Table S4: Lowest energy levels in cm^{-1} for Pr-acac$_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^3H_4$	0.000	0.000	0.000	0.000	0.000
2		30.044	35.422	35.337	35.144	35.228
3		245.415	257.721	258.120	258.042	257.645
4		323.248	335.834	336.136	335.976	335.677
5		351.058	372.879	373.300	372.979	372.561
6		432.155	454.142	454.707	454.443	453.868
7		463.804	479.552	480.057	479.947	479.445
8		554.146	572.214	573.088	572.854	571.979
9		560.293	578.304	579.185	578.930	578.044
10	$^3H_5$	5100.211	2268.720	2269.091	2261.752	2261.384
11		5101.345	2272.403	2272.775	2265.458	2265.087
12		5313.022	2490.227	2490.486	2483.208	2482.955
13		5342.852	2515.782	2516.078	2508.754	2508.467
14		5404.147	2576.737	2576.882	2569.604	2569.465
15		5447.364	2618.922	2619.038	2611.744	2611.629
16		5477.411	2649.229	2649.455	2642.120	2641.904
17		5529.861	2696.860	2696.933	2689.586	2689.510
18		5536.870	2713.352	2713.432	2706.145	2706.066
19		5631.764	2796.512	2796.416	2789.012	2789.110
20		5639.174	2803.905	2803.813	2796.425	2796.518

Table S5: Lowest energy levels in cm^{-1} for Nd-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^4I_{9/2}$	0.000	0.000	0.000	0.000	0.000
2		119.087	123.800	124.312	124.328	123.791
3		183.426	199.307	199.927	199.896	199.263
4		240.237	257.802	258.261	258.306	257.816
5		293.518	313.924	314.829	314.815	313.880
6	$^4I_{11/2}$	4537.869	1996.989	1997.329	1968.895	1968.565
7		4618.762	2079.781	2080.100	2051.724	2051.389
8		4670.952	2131.587	2131.841	2103.463	2103.198
9		4691.019	2151.582	2151.831	2123.401	2123.149
10		4710.870	2172.357	2172.616	2144.278	2144.002
11		4770.697	2232.022	2232.165	2203.795	2203.635

Table S6: Lowest energy levels in cm^{-1} for Sm-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{5/2}$	0.000	0.000	0.000	0.000	0.000
2		177.622	177.085	176.653	177.167	177.607
3		305.772	312.792	312.168	312.320	312.954
4	$^6H_{7/2}$	2711.292	1089.569	1089.078	1049.252	1049.762
5		2851.411	1225.692	1225.172	1185.704	1186.243
6		2912.850	1289.108	1288.577	1249.163	1249.715
7		2994.362	1368.264	1367.810	1328.289	1328.763

Table S7: Lowest energy levels in cm^{-1} for Eu-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^7F_0$	0.000	0.000	0.000	0.000	0.000
2	$^7F_1$	1373.933	246.339	246.501	234.193	234.032
3		1518.521	401.216	401.186	388.828	388.870
4		1625.032	521.864	521.534	509.521	509.846
5	$^7F_2$	3406.539	961.186	961.265	924.811	924.737
6		3454.265	983.695	983.817	945.829	945.719
7		3556.923	1096.882	1096.698	1058.859	1059.060
8		3604.152	1152.722	1152.520	1115.540	1115.747
9		3638.359	1186.961	1186.467	1149.357	1149.852
10	$^7F_3$	5648.331	1924.055	1924.354	1848.650	1848.379
11		5660.111	1936.855	1937.045	1861.213	1861.088
12		5662.126	1938.488	1938.100	1862.530	1862.905
13		5687.503	1971.047	1970.584	1894.931	1895.409
14		5698.096	1989.560	1989.385	1915.053	1915.229
15		5738.170	2022.017	2021.579	1946.689	1947.123
16		5759.521	2038.474	2038.099	1962.630	1963.021
17	$^7F_4$	7698.420	2878.274	2878.084	2751.521	2751.729
18		7753.565	2928.207	2927.975	2800.857	2801.122
19		7773.922	2945.039	2944.588	2817.105	2817.570
20		7796.118	2966.115	2965.796	2837.764	2838.124
21		7821.712	3012.699	3012.270	2886.686	2887.136
22		7859.958	3039.070	3038.822	2912.385	2912.643
23		7884.314	3066.512	3066.143	2939.921	2940.305
24		7936.953	3116.137	3116.228	2989.366	2989.306
25		7951.923	3131.608	3131.621	3004.739	3004.753
26	$^7F_5$	9727.458	3991.868	3990.845	3797.194	3798.258
27		9731.709	3996.273	3995.287	3801.704	3802.730
28		9770.927	4039.874	4039.547	3846.778	3847.155
29		9781.244	4049.099	4048.848	3855.829	3856.132
30		9840.859	4126.938	4126.616	3935.898	3936.234
31		9856.045	4136.070	4135.768	3944.368	3944.688
32		9891.138	4174.527	4174.319	3983.094	3983.306
33		9902.187	4182.124	4182.195	3990.774	3990.727
34		9930.034	4210.433	4210.372	4018.753	4018.831
35		10018.426	4296.588	4296.775	4104.697	4104.565
36		10022.203	4300.427	4300.618	4108.492	4108.354
37	$^7F_6$	11422.275	5034.872	5033.739	4762.134	4763.308
38		11422.362	5034.987	5033.853	4762.257	4763.430
39		11621.991	5250.835	5250.075	4979.670	4980.461

40	11622.858	5251.765	5251.012	4980.614	4981.397
41	11704.953	5329.951	5329.414	5057.497	5058.056
42	11709.872	5336.197	5335.765	5064.059	5064.518
43	11741.869	5367.412	5367.038	5094.764	5095.158
44	11767.201	5394.999	5394.914	5122.833	5122.960
45	11773.721	5401.445	5401.334	5129.101	5129.252
46	11812.475	5438.815	5438.578	5165.739	5166.027
47	11812.652	5439.041	5438.795	5165.955	5166.253
48	11880.090	5506.517	5507.583	5234.450	5233.441
49	11880.162	5506.587	5507.653	5234.517	5233.508

Table S8: Lowest energy levels in cm^{-1} for Gd-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^8H_{7/2}$	0.000	0.000	0.000	0.000	0.000
2		1.198	0.256	0.240	0.240	0.256
3		2.329	0.534	0.466	0.465	0.534
4		4.320	0.978	0.820	0.820	0.978
5	$^6P_{7/2}$	35631.422	38754.739	38755.034	38742.438	38742.153
6		35687.191	38791.917	38792.152	38779.474	38779.248
7		35728.649	38819.803	38819.965	38807.179	38807.027
8		35822.180	38862.123	38862.141	38849.166	38849.156

Table S9: Lowest energy levels in cm^{-1} for Tb-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{\mathrm{SO}}^{(1)}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{MF}}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{AMF}}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{ABP}}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{BP}}$
1	$^7F_6$	0.000	0.000	0.000	0.000	0.000
2		0.086	0.088	0.088	0.089	0.089
3		109.166	110.230	110.745	110.994	110.466
4		109.498	110.721	111.240	111.488	110.955
5		178.742	175.074	175.694	176.244	175.607
6		181.252	177.079	177.679	178.232	177.615
7		251.493	249.227	249.974	250.728	249.955
8		274.771	270.802	271.533	272.333	271.578
9		302.233	301.949	302.774	303.449	302.595
10		382.280	372.479	373.349	374.708	373.811
11		385.096	376.714	377.600	378.854	377.941
12		598.843	609.223	610.352	611.159	610.007
13		598.918	609.364	610.494	611.296	610.143
14	$^7F_5$	4578.634	2134.613	2134.871	2221.242	2220.953
15		4581.181	2137.687	2137.938	2224.307	2224.024
16		4709.263	2264.358	2264.789	2351.952	2351.479
17		4729.411	2285.391	2285.791	2372.912	2372.478
18		4754.032	2306.305	2306.825	2394.257	2393.687
19		4790.102	2342.268	2342.862	2430.763	2430.125
20		4800.710	2358.785	2359.322	2446.743	2446.169
21		4841.647	2413.206	2413.719	2500.278	2499.730
22		4843.614	2415.628	2416.174	2502.618	2502.035
23		4936.468	2506.351	2507.343	2593.697	2592.669
24		4941.254	2511.618	2512.609	2598.894	2597.867

Table S10: Lowest energy levels in cm^{-1} for Dy-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		150.012	155.631	155.926	156.224	155.919
3		227.942	233.726	234.178	234.441	233.973
4		279.416	287.084	287.655	287.940	287.350
5		308.225	316.519	317.365	317.671	316.802
6		392.191	408.291	409.277	409.614	408.606
7		441.406	462.929	463.280	463.546	463.192
8		504.802	527.901	529.371	529.712	528.218
9	$^6H_{13/2}$	7590.741	3604.472	3604.306	3720.021	3720.180
10		7667.916	3681.367	3681.459	3797.518	3797.394
11		7744.439	3760.008	3760.295	3876.349	3876.011
12		7789.661	3806.445	3806.795	3922.803	3922.396
13		7833.079	3853.451	3853.829	3969.690	3969.251
14		7868.779	3891.231	3891.794	4007.600	4006.987
15		7927.175	3949.623	3950.773	4066.627	4065.433

Table S11: Lowest energy levels in cm^{-1} for Dy-acac$_3$-dppz, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		140.260	146.058	146.238	146.525	146.334
3		216.017	220.812	221.069	221.339	221.062
4		252.616	258.739	258.929	259.182	258.961
5		284.484	294.399	294.613	294.884	294.643
6		331.070	347.807	347.545	347.798	348.046
7		389.570	407.767	408.196	408.522	408.059
8		482.724	507.087	507.844	508.170	507.399
9	$^6H_{13/2}$	7578.824	3593.847	3593.496	3709.120	3709.457
10		7662.257	3676.720	3676.694	3792.632	3792.626
11		7735.159	3752.413	3752.448	3868.375	3868.289
12		7763.013	3782.877	3782.624	3898.441	3898.637
13		7799.203	3817.762	3817.716	3933.601	3933.597
14		7820.567	3842.565	3842.681	3958.441	3958.256
15		7864.291	3889.519	3889.862	4005.493	4005.088

Table S12: Lowest energy levels in cm^{-1} for Dy-acac$_3$-dpq, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{\mathrm{SO}}^{(1)}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{MF}}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{AMF}}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{ABP}}$	$\mathcal{H}_{\mathrm{SO}}^{\mathrm{BP}}$
1	$^6\mathrm{H}_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		115.823	121.063	121.091	121.300	121.265
3		183.165	188.351	188.291	188.503	188.549
4		219.752	225.325	225.250	225.483	225.539
5		259.673	267.290	267.295	267.586	267.560
6		279.837	291.320	291.175	291.433	291.563
7		385.096	404.242	404.679	404.986	404.516
8		515.146	540.573	540.678	540.984	540.875
9	$^6\mathrm{H}_{13/2}$	7561.693	3574.656	3574.412	3690.108	3690.334
10		7647.109	3660.830	3660.653	3776.558	3776.709
11		7698.455	3714.005	3713.662	3829.550	3829.849
12		7725.342	3742.333	3741.930	3857.782	3858.137
13		7771.694	3788.416	3788.278	3904.199	3904.284
14		7812.332	3833.729	3833.726	3949.506	3949.458
15		7893.439	3919.229	3919.106	4034.756	4034.821

Table S13: Lowest energy levels in cm^{-1} for Dy-acac$_3$-phen, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		123.698	129.729	129.951	130.197	129.963
3		193.171	198.917	199.001	199.249	199.149
4		244.202	250.050	250.095	250.340	250.270
5		284.896	292.441	292.697	292.986	292.695
6		320.482	337.056	336.694	336.955	337.298
7		405.817	425.197	425.920	426.274	425.509
8		493.610	517.999	519.016	519.358	518.314
9	$^6H_{13/2}$	7567.171	3581.339	3580.932	3696.600	3696.986
10		7650.893	3664.519	3664.507	3780.435	3780.414
11		7718.129	3734.289	3734.242	3850.170	3850.170
12		7755.668	3774.985	3774.499	3890.331	3890.759
13		7792.445	3811.010	3811.021	3926.910	3926.838
14		7830.099	3852.449	3852.806	3968.569	3968.141
15		7888.933	3912.703	3913.335	4029.106	4028.407

Table S14: Lowest energy levels in cm^{-1} for Dy-hfac$_3$-glyme, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		105.036	108.469	108.605	108.768	108.627
3		156.141	157.833	158.129	158.300	157.993
4		182.523	186.353	186.838	187.023	186.523
5		210.550	218.292	218.160	218.300	218.428
6		239.918	249.820	250.098	250.292	250.000
7		300.513	313.612	314.499	314.743	313.831
8		428.731	450.082	451.792	452.086	450.360
9	$^6H_{13/2}$	7547.744	3558.825	3558.305	3673.997	3674.502
10		7628.518	3639.850	3639.693	3755.570	3755.696
11		7670.593	3684.425	3684.138	3799.947	3800.201
12		7692.455	3705.553	3705.504	3821.370	3821.375
13		7729.002	3742.389	3742.794	3858.691	3858.238
14		7753.931	3769.822	3770.476	3886.304	3885.593
15		7807.296	3827.080	3828.392	3944.047	3942.673

Table S15: Lowest energy levels in cm^{-1} for Dy-trensal, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O and N, [3s2p] for C, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		30.532	28.562	28.583	28.657	28.635
3		77.086	69.843	69.927	69.998	69.906
4		153.117	145.131	145.382	145.604	145.331
5		306.436	313.409	313.666	313.918	313.653
6		405.853	416.679	416.949	417.287	417.013
7		467.548	479.501	479.873	480.526	480.142
8		632.417	664.100	664.873	665.695	664.883
9	$^6H_{13/2}$	7576.211	3589.180	3588.990	3704.767	3704.955
10		7602.143	3614.904	3614.734	3730.460	3730.619
11		7615.016	3632.699	3632.623	3748.059	3748.119
12		7741.450	3766.543	3766.358	3881.795	3881.926
13		7793.046	3824.058	3824.101	3939.366	3939.271
14		7894.758	3914.115	3914.361	4030.384	4030.077
15		7935.145	3963.457	3963.967	4079.887	4079.295

Table S16: Lowest energy levels in cm^{-1} for Dy-paah$_2$-$(NO_3)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		109.198	110.283	110.416	110.556	110.409
3		192.180	193.223	193.518	193.749	193.424
4		247.590	251.089	251.523	251.809	251.334
5		297.334	311.742	312.689	312.944	311.951
6		325.382	340.487	341.296	341.611	340.762
7		373.400	390.952	391.449	391.786	391.250
8		409.699	433.665	434.412	434.799	434.005
9	$^6H_{13/2}$	7545.738	3557.050	3556.885	3672.583	3672.721
10		7650.197	3663.305	3663.254	3779.144	3779.144
11		7714.155	3728.925	3728.985	3844.923	3844.795
12		7753.580	3770.906	3771.287	3887.163	3886.710
13		7794.618	3811.331	3811.634	3927.572	3927.200
14		7824.415	3843.471	3843.933	3959.780	3959.238
15		7846.033	3864.461	3865.070	3980.904	3980.228

Table S17: Lowest energy levels in cm^{-1} for Dy-tta_3-phen, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for N and O, [3s2p] for C, F, and S, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		117.665	122.997	123.231	123.458	123.210
3		166.787	169.195	169.554	169.741	169.357
4		203.114	206.342	206.939	207.192	206.561
5		227.402	234.548	234.952	235.179	234.746
6		265.610	275.016	275.521	275.786	275.248
7		361.611	377.794	378.772	379.123	378.100
8		487.695	511.291	512.400	512.745	511.614
9	$^6H_{13/2}$	7553.139	3565.672	3565.383	3681.050	3681.312
10		7634.731	3646.460	3646.441	3762.354	3762.334
11		7689.971	3704.977	3704.988	3820.811	3820.746
12		7715.653	3730.283	3730.524	3846.432	3846.140
13		7760.726	3775.687	3776.148	3892.111	3891.592
14		7788.348	3807.378	3808.035	3923.867	3923.136
15		7856.250	3879.738	3880.589	3996.229	3995.301

Table S18: Lowest energy levels in cm^{-1} for Dy-tta_3-bipy, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for N and O, [3s2p] for C, F, and S, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^6H_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		130.105	135.951	136.005	136.165	136.096
3		147.499	152.480	152.834	153.091	152.724
4		187.634	192.431	192.603	192.815	192.626
5		218.189	225.365	225.264	225.471	225.559
6		268.511	280.652	281.054	281.322	280.893
7		360.112	376.932	377.729	378.070	377.237
8		429.879	451.812	453.789	454.149	452.146
9	$^6H_{13/2}$	7559.534	3574.052	3573.339	3688.962	3689.655
10		7635.883	3649.515	3649.194	3765.036	3765.323
11		7672.084	3688.366	3688.082	3803.845	3804.093
12		7717.070	3732.728	3732.840	3848.717	3848.560
13		7743.719	3759.812	3760.521	3876.502	3875.744
14		7783.997	3804.852	3805.502	3921.229	3920.504
15		7809.158	3829.661	3830.967	3946.705	3945.324

Table S19: Lowest energy levels in cm^{-1} for Ho-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^5I_8$	0.000	0.000	0.000	0.000	0.000
2		1.919	2.182	2.140	2.147	2.190
3		46.129	50.707	51.257	51.368	50.787
4		52.377	58.020	58.590	58.714	58.117
5		84.145	93.831	94.794	95.001	94.013
6		108.648	122.029	123.069	123.319	122.255
7		129.353	144.360	145.815	146.136	144.645
8		142.483	159.688	160.937	161.270	159.981
9		149.947	167.620	168.593	168.957	167.933
10		165.937	185.877	186.440	186.840	186.228
11		182.349	204.311	205.442	205.871	204.680
12		190.878	212.945	214.624	215.061	213.305
13		197.172	219.965	221.302	221.774	220.362
14		206.744	231.834	232.292	232.771	232.246
15		220.600	247.650	248.364	248.888	248.109
16		251.539	282.228	284.298	284.909	282.779
17		252.224	283.145	285.208	285.821	283.699
18	$^5I_7$	10504.775	5158.213	5158.016	5276.684	5276.792
19		10504.879	5158.382	5158.183	5276.851	5276.962
20		10552.648	5208.799	5209.058	5327.730	5327.393
21		10553.927	5210.656	5210.902	5329.574	5329.249
22		10586.377	5244.056	5244.654	5363.403	5362.728
23		10593.621	5252.806	5253.363	5372.110	5371.482
24		10599.377	5258.857	5259.545	5378.293	5377.520
25		10607.311	5267.616	5268.188	5386.907	5386.256
26		10614.533	5275.319	5276.007	5394.734	5393.974
27		10618.157	5279.770	5279.788	5398.482	5398.405
28		10621.291	5283.129	5283.250	5401.952	5401.773
29		10628.557	5289.912	5291.177	5409.923	5408.578
30		10629.669	5291.149	5292.406	5411.152	5409.817
31		10678.232	5342.224	5344.069	5462.801	5460.893
32		10678.298	5342.304	5344.149	5462.881	5460.973

Table S20: Lowest energy levels in cm^{-1} for Er-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^4I_{15/2}$	0.000	0.000	0.000	0.000	0.000
2		36.831	37.218	36.034	36.052	37.255
3		74.791	73.151	72.775	72.820	73.200
4		100.935	97.498	96.568	96.576	97.505
5		136.949	137.747	137.332	137.469	137.864
6		184.714	183.265	182.466	182.581	183.347
7		266.129	262.179	260.916	261.015	262.248
8		323.567	316.769	314.869	314.921	316.775
9	$^4I_{13/2}$	12759.303	6612.572	6612.129	6693.212	6693.604
10		12789.242	6642.180	6640.532	6721.613	6723.204
11		12819.419	6671.957	6671.104	6752.167	6752.985
12		12836.205	6688.354	6687.029	6768.101	6769.386
13		12868.241	6720.243	6718.951	6799.999	6801.262
14		12924.615	6775.984	6774.444	6855.483	6856.993
15		12984.987	6834.685	6832.727	6913.722	6915.667

Table S21: Lowest energy levels in cm^{-1} for Tm-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^3H_6$	0.000	0.000	0.000	0.000	0.000
2		0.710	0.713	0.721	0.721	0.713
3		137.511	139.317	138.485	138.560	139.389
4		141.074	142.578	141.713	141.782	142.644
5		188.034	188.855	187.311	187.372	188.912
6		202.109	202.194	200.521	200.569	202.236
7		253.536	253.171	251.595	251.655	253.222
8		305.557	304.046	302.132	302.179	304.083
9		321.478	320.195	318.348	318.396	320.231
10		427.783	424.983	422.620	422.658	425.008
11		428.420	425.746	423.402	423.440	425.771
12		634.833	632.315	629.472	629.552	632.376
13		634.905	632.398	629.553	629.632	632.459
14	$^3H_5$	6457.523	6900.916	6899.561	6958.324	6959.676
15		6498.903	6944.529	6943.114	7000.986	7002.398
16		6538.608	6976.716	6974.969	7034.027	7035.750
17		6544.062	6991.190	6989.564	7047.778	7049.388
18		6592.535	7032.458	7030.819	7089.153	7090.769
19		6641.845	7100.982	7099.326	7156.263	7157.873
20		6660.412	7121.374	7119.760	7175.855	7177.438
21		6711.782	7149.517	7147.674	7205.678	7207.474
22		6725.750	7173.261	7171.467	7228.504	7230.260
23		15519.004	8360.321	8358.678	8390.166	8391.800
24		15519.434	8361.362	8359.721	8391.226	8392.858

Table S22: Lowest energy levels in cm^{-1} for Yb-$acac_3$-$(H_2O)_2$, estimated using different approximations to spin-orbit coupling Hamiltonian. Computation at CAHF/CASCI-SO level on ANO-RCC basis set, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
1	$^2F_{7/2}$	0.000	0.000	0.000	0.000	0.000
2		210.998	208.998	208.662	208.661	208.988
3		253.015	251.256	250.563	250.563	251.250
4		360.947	359.358	358.009	358.010	359.345
5	$^2F_{5/2}$	19085.144	10611.114	10609.584	10581.883	10583.408
6		19259.737	10787.325	10786.045	10758.341	10759.617
7		19372.892	10900.917	10900.108	10872.402	10873.215