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Electron correlation effects of the ThO and ThS molecules in the spinor basis. A relativistic coupled cluster study of the ground and excited states properties.

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Supplementary Information

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1 Fock space coupled cluster: computational details

In both molecules the $7s$, $6d$, and $7p$ spinors were included in the model (P_i) space.

Table S1: A detailed description of active spaces used in the IH-FSCCSD calculations for the ThO molecule.

Method/ basis	inactive occupied	active occupied	active virtual	inactive virtual	P_i occupied (E_h)	P_i virtual(E_h)
IHFSCC(1,1)/dyall.v3z	18	16	22	354	$[-10.00;-0.30]$	[0.08;0.011]
IHFSCC(0,2)/dyall.v3z	36	0	24	350	–	$[-0.30;-0.20]$

Table S2: A detailed description of active spaces used in the IH-FSCCSD calculations for the ThS molecule.

Method/ basis	inactive occupied	active occupied	active virtual	inactive virtual	P_i occupied (E_h)	P_i virtual (E_h)
IHFSCC(1,1)/dyall.v3z	18	16	12	352	$[-7.0;-0.30]$	[0.07;0.13]
IHFSCC(0,2)/dyall.v3z	36	0	15	348	–	$[-0.30;-0.20]$

2 IHFSCC total energies

Table S3: IHFSCC total energies for ThO (in E_h).

r_e [Å]	X 0^+	1 (H)	2 (Q)	3 (W)	0^-	0^+ (A)	1 (B)	2	1 (C)	2	1 (D)	0^-	0^+ (E)
IHFSCC(1,1)													
1.74	−26592.427902	−26592.397888	−26592.393839	−26592.386774	−26592.371454	−26592.369036		−26592.364276		−26592.352366			
1.76	−26592.427902	−26592.402037	−26592.397962	−26592.390850	−26592.375748	−26592.373304		−26592.368181		−26592.356637			
1.78	−26592.430582	−26592.405243	−26592.401143	−26592.393985	−26592.379109	−26592.376642		−26592.371157		−26592.359975			
1.80	−26592.432383	−26592.407580	−26592.403458	−26592.396253	−26592.381788	−26592.377489		−26592.373280	−26592.364213	−26592.362451			
1.82	−26592.433377	−26592.409121	−26592.404975	−26592.397724	−26592.383517	−26592.379131		−26592.374620	−26592.366105	−26592.364140		−26592.366351	−26592.352779
1.84	−26592.433629	−26592.409929	−26592.405760	−26592.398463	−26592.384527	−26592.380057		−26592.375240	−26592.367270	−26592.365101		−26592.367567	−26592.354573
1.86	−26592.433202	−26592.410063	−26592.405872	−26592.398530	−26592.384877	−26592.380327		−26592.375202	−26592.367767	−26592.365395		−26592.368117	−26592.355701
1.88	−26592.432152	−26592.409579	−26592.405366	−26592.397979	−26592.384623	−26592.379998		−26592.374560	−26592.367651	−26592.365075		−26592.368055	−26592.356215
1.90	−26592.430532	−26592.408529	−26592.404294	−26592.396861	−26592.383818	−26592.379121		−26592.373366	−26592.366973	−26592.364191		−26592.367432	−26592.356163
1.92	−26592.428391	−26592.406958	−26592.402702	−26592.395225	−26592.382511	−26592.377746		−26592.371669	−26592.365782	−26592.362790		−26592.366295	−26592.355592
1.94	−26592.425773	−26592.404913	−26592.400637	−26592.393115	−26592.380745	−26592.375918		−26592.369513	−26592.364120	−26592.360915		−26592.364690	−26592.354543
1.96	−26592.422723	−26592.402435	−26592.398137	−26592.390571	−26592.378563	−26592.373680		−26592.366940	−26592.362030	−26592.358604		−26592.362658	−26592.353056
IHFSCC(0,2)													
1.76	−26592.379733	−26592.350318	−26592.346563	−26592.339663	−26592.327650	−26592.325918	−26592.322197	−26592.320304	−26592.302628	−26592.311241	−26592.296273	−26592.298483	−26592.293751
1.78	−26592.382462	−26592.353548	−26592.349768	−26592.342811	−26592.330959	−26592.329225	−26592.325553	−26592.323395	−26592.306122	−26592.314532	−26592.299725	−26592.301806	−26592.297258
1.80	−26592.384399	−26592.355913	−26592.352108	−26592.345094	−26592.333402	−26592.331668	−26592.328043	−26592.325628	−26592.308756	−26592.316956	−26592.302310	−26592.304272	−26592.300021
1.82	−26592.385525	−26592.357480	−26592.353651	−26592.346580	−26592.335046	−26592.333312	−26592.329735	−26592.327072	−26592.310596	−26592.318581	−26592.304095	−26592.305948	−26592.301987
1.84	−26592.385905	−26592.358314	−26592.354461	−26592.347335	−26592.335954	−26592.334221	−26592.330693	−26592.327791	−26592.311706	−26592.319470	−26592.305144	−26592.306896	−26592.303219
1.86	−26592.385601	−26592.358473	−26592.354597	−26592.347416	−26592.336187	−26592.334453	−26592.330975	−26592.327842	−26592.312141	−26592.319683	−26592.305516	−26592.307174	−26592.303777
1.88	−26592.384669	−26592.358012	−26592.354114	−26592.346878	−26592.335796	−26592.334063	−26592.330634	−26592.327280	−26592.311955	−26592.319274	−26592.305266	−26592.306837	−26592.303714
1.90	−26592.383163	−26592.356982	−26592.353061	−26592.345772	−26592.334834	−26592.333101	−26592.329721	−26592.326155	−26592.311197	−26592.318291	−26592.304442	−26592.305932	−26592.303081
1.92	−26592.381129	−26592.355428	−26592.351486	−26592.344144	−26592.333345	−26592.331613	−26592.328282	−26592.324513	−26592.309913	−26592.316783	−26592.303093	−26592.304507	−26592.301924

Table S4: IHFSCC total energies for ThS (in E_h).

r_e [Å]	X 0^+	1	2	3	0^-	0^+	1	2	2	1	0^-	0^+
IHFSCC(1,1)												
2.28	−26915.941297	−26915.927207	−26915.922587	−26915.915034			−26915.887693	−26915.879239				
2.30	−26915.942500	−26915.928946	−26915.924316	−26915.916720			−26915.889502	−26915.881375				
2.32	−26915.943257	−26915.930235	−26915.925594	−26915.917957	−26915.901068	−26915.899224	−26915.890884	−26915.883037			−26915.866635	−26915.866635
2.34	−26915.943601	−26915.931106	−26915.926454	−26915.918774	−26915.902298	−26915.900493	−26915.891877	−26915.884282			−26915.868110	−26915.868110
2.36	−26915.943561	−26915.931587	−26915.926924	−26915.919200	−26915.903146	−26915.901383	−26915.892510	−26915.885118			−26915.869188	−26915.869188
2.38	−26915.943164	−26915.931705	−26915.927031	−26915.919263	−26915.903638	−26915.901919	−26915.892813	−26915.885566			−26915.869896	−26915.869896
2.40	−26915.942435	−26915.931484	−26915.926800	−26915.918986	−26915.903797	−26915.902125	−26915.892813	−26915.885648			−26915.870259	−26915.870259
2.42	−26915.941399	−26915.930950	−26915.926255	−26915.918396	−26915.903646	−26915.902023	−26915.892535	−26915.885384			−26915.870300	−26915.870300
2.44	−26915.940079	−26915.930125	−26915.925418	−26915.917513	−26915.903206	−26915.901634	−26915.892000	−26915.884795			−26915.870042	−26915.870042
IHFSCC(0,2)												
2.26	−26916.085623	−26916.062365	−26916.058120	−26916.050957	−26916.037115	−26916.035657	−26916.032240	−26916.027437	−26916.019367	−26916.014250	−26916.009399	−26916.004987
2.28	−26916.087272	−26916.064475	−26916.060217	−26916.053006	−26916.039408	−26916.037942	−26916.034586	−26916.029575	−26916.021660	−26916.016769	−26916.011982	−26916.007547
2.30	−26916.088434	−26916.066095	−26916.061823	−26916.054565	−26916.041204	−26916.039730	−26916.036436	−26916.031229	−26916.023457	−26916.018787	−26916.014068	−26916.009604
2.32	−26916.089145	−26916.067256	−26916.062972	−26916.055668	−26916.042535	−26916.041054	−26916.037820	−26916.032428	−26916.024791	−26916.020334	−26916.015691	−26916.011191
2.34	−26916.089442	−26916.068109	−26916.063809	−26916.056449	−26916.043591	−26916.042100	−26916.038942	−26916.033333	−26916.025853	−26916.021655	−26916.017109	−26916.012560
2.36	−26916.089327	−26916.068323	−26916.064013	−26916.056620	−26916.043922	−26916.042426	−26916.039312	−26916.033581	−26916.026188	−26916.022142	−26916.017656	−26916.013075
2.38	−26916.088855	−26916.068282	−26916.063960	−26916.056523	−26916.044033	−26916.042530	−26916.039476	−26916.033588	−26916.026307	−26916.022457	−26916.018053	−26916.013428
2.40	−26916.088042	−26916.067892	−26916.063558	−26916.056078	−26916.043790	−26916.042279	−26916.039284	−26916.033249	−26916.026073	−26916.022414	−26916.018092	−26916.013421
2.42	−26916.086912	−26916.067177	−26916.062831	−26916.055309	−26916.043217	−26916.041699	−26916.038761	−26916.032587	−26916.025511	−26916.022037	−26916.017797	−26916.013079
2.44	−26916.085487	−26916.066157	−26916.061800	−26916.054236	−26916.042335	−26916.040810	−26916.037930	−26916.031623	−26916.024642	−26916.021348	−26916.017189	−26916.012425

Table S 5: Composition of the wave function for the ThO model IHFSCC(1,1) and IHFSCC(0,2) spaces. The assignment to the σ, π, δ, etc. is based on the Mullikan population analysis of the DHF spinors and should be considered as very approximate.

State	IHFSCC(1,1)	IHFSCC(0,2)
1 (H)	99% $\frac{1}{2}\sigma\frac{3}{2}\delta$	99% $\frac{1}{2}\sigma\frac{3}{2}\delta$
2 (Q)	69% $\frac{1}{2}\sigma\frac{3}{2}\delta$ + 29% $\frac{1}{2}\sigma\frac{5}{2}\delta$	71% $\frac{1}{2}\sigma\frac{3}{2}\delta$ + 28% $\frac{1}{2}\sigma\frac{5}{2}\delta$
3 (W)	100% $\frac{1}{2}\sigma\frac{5}{2}\delta$	99% $\frac{1}{2}\sigma\frac{5}{2}\delta$
0^-	42% $\frac{1}{2}\sigma\frac{1}{2}\pi$ + 40% $\frac{1}{2}\sigma\frac{1}{2}\pi'$	98% $\frac{1}{2}\sigma\frac{1}{2}\delta$
0^+(A)	56% $\frac{1}{2}\sigma\frac{1}{2}\pi$ + 42% $\frac{1}{2}\sigma\frac{1}{2}\pi'$	98% $\frac{1}{2}\sigma\frac{1}{2}\delta$
2	66% $\frac{1}{2}\sigma\frac{5}{2}\delta$ + 24% $\frac{1}{2}\sigma\frac{3}{2}\delta'$	62% $\frac{1}{2}\sigma\frac{5}{2}\delta$ + 20% $\frac{1}{2}\sigma\frac{3}{2}\delta$
1 (C)	73% $\frac{1}{2}\sigma\frac{1}{2}\sigma'$ + 9% $\frac{1}{2}\sigma\frac{1}{2}\delta''$	77% $\frac{1}{2}\sigma\frac{1}{2}\delta$ + 17% $\frac{1}{2}\sigma\frac{3}{2}\delta'$
2	52% $\frac{1}{2}\sigma\frac{3}{2}\delta$ + 36% $\frac{1}{2}\sigma\frac{3}{2}\delta'$	89% $\frac{1}{2}\sigma\frac{3}{2}\delta$
0^-	85% $\frac{1}{2}\sigma\frac{1}{2}\delta'$	98% $\frac{1}{2}\sigma\frac{1}{2}\delta'$
0^+(E)	84% $\frac{1}{2}\sigma\frac{1}{2}\delta'$	48% $\frac{1}{2}\sigma\frac{3}{2}\delta$+45% $\frac{1}{2}\sigma\frac{1}{2}\delta'$

Table S 6: Composition of the wave function for the ThS model IHFSCC(1,1) and IHFSCC(0,2) spaces. The assignment to the σ, π, δ, etc. is based on the Mullikan population analysis of the DHF spinors and should be considered as very approximate.

State	IHFSCC(1,1)	IHFSCC(0,2)
1	97% $\frac{1}{2}\sigma\frac{3}{2}\delta$	99% $\frac{1}{2}\sigma\frac{3}{2}\delta$
2	66% $\frac{1}{2}\sigma\frac{3}{2}\delta$ + 31% $\frac{1}{2}\sigma\frac{5}{2}\delta$	69% $\frac{1}{2}\sigma\frac{3}{2}\delta$ + 30% $\frac{1}{2}\sigma\frac{5}{2}\delta$
3	100% $\frac{1}{2}\sigma\frac{5}{2}\delta$	100% $\frac{1}{2}\sigma\frac{5}{2}\delta$
0^-	70% $\frac{1}{2}\sigma\frac{1}{2}\pi$ + 26% $\frac{1}{2}\sigma\frac{1}{2}\pi'$	97% $\frac{1}{2}\sigma\frac{1}{2}\sigma'$
0^+	67% $\frac{1}{2}\sigma\frac{1}{2}\pi$ + 25% $\frac{1}{2}\sigma\frac{1}{2}\pi'$	97% $\frac{1}{2}\sigma\frac{1}{2}\sigma'$
2	53% $\frac{1}{2}\sigma\frac{3}{2}\delta'$ +16% $\frac{1}{2}\sigma\frac{3}{2}\pi$ +12% $\frac{1}{2}\sigma\frac{3}{2}\delta''$	56% $\frac{1}{2}\sigma\frac{5}{2}\delta$+21% $\frac{1}{2}\sigma\frac{3}{2}\delta$+ +12% $\frac{1}{2}\sigma\frac{3}{2}\delta'$
2	35% $\frac{1}{2}\sigma\frac{3}{2}\delta'$ +32% $\frac{1}{2}\sigma\frac{3}{2}\pi$ +12% $\frac{1}{2}\sigma\frac{3}{2}\delta''$	85% $\frac{1}{2}\sigma\frac{3}{2}\delta'$
0^-	56% $\frac{1}{2}\sigma\frac{1}{2}\sigma'$+38% $\frac{1}{2}\sigma\frac{1}{2}\sigma''$	68% $\frac{3}{2}\delta\frac{3}{2}\delta$ +21% $\frac{1}{2}\sigma\frac{1}{2}\sigma'$
0^+	50% $\frac{1}{2}\sigma\frac{1}{2}\sigma'$+38% $\frac{1}{2}\sigma\frac{1}{2}\sigma''$	98% $\frac{1}{2}\sigma\frac{1}{2}\sigma'$