

A configuration interaction correction on top of pair coupled cluster doubles

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Supplementary Information

S1 Matrix elements of the pCCD-CI methods

All the following matrix elements of the pCCD-CI methods are in their spin-free formulation. Within the Davidson method, the diagonalization of \mathbf{H} reduces to a simpler matrix–vector product of the form

$$\sigma_i = \mathbf{H}b_i, \quad (1)$$

where $\{b_i\}$ are (orthonormal) trial vectors and the number of elements in the b vectors equals the number of configurations $\{\Phi_\mu\}$ entering the CI expansion. Thus, to obtain the pCCD-CI working equations, we need to determine the different blocks of the σ vector for the pCCD-CIS, pCCD-CID, and pCCD-CISD models. In the following, we abbreviate $\mathcal{H}^{(p)}$ by \mathcal{H} .

S1.1 pCCD-CIS

The σ vector of pCCD-CIS contains the following elements, where $\{c_0, c_K^C\}$ indicates the current approximation to the CI coefficients (Einstein summation convention over repeated indices is assumed),

$$\text{pCCD-CIS } \sigma_0 = \langle \Phi_0 | \mathcal{H} | \Phi_K^C \rangle c_K^C = 2f_{KC}c_K^C \quad (2)$$

and

$$\begin{aligned} \text{pCCD-CIS } \sigma_I^A &= \langle \Phi_I^A | \mathcal{H} | \Phi_0 \rangle c_0 + \langle \Phi_I^A | \mathcal{H} | \Phi_K^C \rangle c_K^C \\ &= [f_{IA} + f_{IA}t_{II}^{AA} + \langle AI|CC \rangle t_{II}^{CC} + \langle KK|IA \rangle t_{KK}^{AA}] c_0 \\ &\quad + f_{AC}c_I^C - f_{KI}c_K^C + L_{KACI}c_K^C \\ &\quad + L_{ILAD}t_{II}^{AA}c_L^D - \langle IL|CC \rangle t_{II}^{CC}c_L^A - \langle KK|AC \rangle t_{KK}^{AA}c_I^C \end{aligned} \quad (3)$$

S1.2 pCCD-CID

The σ vector of pCCD-CID contains the following elements, where $\{c_{KL}^{CD}\}$ indicates the current approximation to the CI coefficients,

$$\text{pCCD-CID } \sigma_0 = \langle \Phi_0 | \mathcal{H} | \Phi_{KL}^{CD} \rangle c_{KL}^{CD} = L_{KLCD}c_{KL}^{CD} \quad (4)$$

$$\text{pCCD-CID } \sigma_{IJ}^{AB} = \langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_0 \rangle c_0 + \langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_{KL}^{CD} \rangle c_{KL}^{CD} \quad (5)$$

where

$$\begin{aligned} \langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_0 \rangle c_0 &= \langle AB|IJ \rangle c_0 \\ &\quad + P_{IJ}^{AB} \left[f_{BA}t_{II}^{AA} \delta_{IJ} - f_{IJ}t_{II}^{AA} \delta_{AB} \right. \\ &\quad + \frac{1}{2} \langle KK|IJ \rangle t_{KK}^{AA} \delta_{AB} + \frac{1}{2} \langle AB|CC \rangle t_{II}^{CC} \delta_{IJ} \\ &\quad + \langle IB|AJ \rangle t_{II}^{AA} - \langle JB|IA \rangle t_{JJ}^{AA} \\ &\quad + \frac{1}{2} \langle IJ|AB \rangle (t_{II}^{AA}t_{JJ}^{BB} + t_{JJ}^{AA}t_{II}^{BB}) \\ &\quad - \frac{1}{2} \langle IJ|CC \rangle (t_{II}^{CC}t_{JJ}^{AA} + t_{JJ}^{CC}t_{II}^{AA}) \delta_{AB} \\ &\quad - \frac{1}{2} \langle KK|AB \rangle (t_{KK}^{AB}t_{II}^{BB} + t_{KK}^{BB}t_{II}^{AA}) \delta_{IJ} \\ &\quad \left. + \frac{1}{2} \langle KK|CC \rangle (t_{II}^{CC}t_{KK}^{AA}) \delta_{IJ} \delta_{AB} \right] c_0, \end{aligned} \quad (6)$$

and

$$\begin{aligned}
\langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_{KL}^{CD} \rangle c_{KL}^{CD} &= -P_{IJ}^{AB} f_{JK} c_{IK}^{AB} + P_{IJ}^{AB} f_{BC} c_{IJ}^{AC} \\
&+ P_{IJ}^{AB} \left[L_{KACI} c_{JK}^{BC} - \langle KA|CI \rangle c_{JK}^{CB} - \langle KA|JC \rangle c_{IK}^{CB} \right] \\
&+ \frac{1}{2} P_{IJ}^{AB} (\langle AB|CD \rangle c_{IJ}^{CD} + \langle KL|IJ \rangle c_{KL}^{AB}) \\
&+ P_{IJ}^{AB} \left[L_{ILAD} t_{II}^{AA} c_{JL}^{BD} - \langle IL|AD \rangle t_{II}^{AA} c_{JL}^{DB} + \langle IL|CB \rangle t_{II}^{BB} c_{LJ}^{AC} \right] \\
&+ P_{IJ}^{AB} \left[-L_{KICD} t_{II}^{AA} c_{JK}^{DC} \delta_{AB} - L_{KLCA} t_{II}^{AA} c_{LK}^{BC} \delta_{IJ} \right] \\
&+ P_{IJ}^{AB} \left[-\langle IL|CC \rangle t_{II}^{CC} c_{LJ}^{AB} - \langle KK|AD \rangle t_{KK}^{AA} c_{JI}^{BD} \right] \\
&+ \frac{1}{2} P_{IJ}^{AB} \left[\langle KL|CC \rangle t_{II}^{CC} c_{KL}^{AB} \delta_{ij} + \langle KK|CD \rangle t_{KK}^{AA} c_{IJ}^{CD} \delta_{AB} \right] \tag{7}
\end{aligned}$$

with the permutation operator

$$P_{IJ}^{AB} = 1 + P(ij)P(ab),$$

which exchanges the pair of indices (ij) and (ab) with each other, and the shorthand notation

$$L_{KLCD} = 2 \langle KL|CD \rangle - \langle KL|DC \rangle.$$

S1.3 pCCD-CISD

To obtain the working equations of the pCCD-CISD model, eqs. (2) and (3) of pCCD-CIS and eqs. (4), (5), and (7) of pCCD-CID have to be combined and extended with the coupling elements between the singly- and doubly-excited configurations. The coupling terms are as follows

$$\langle \Phi_I^A | \mathcal{H} | \Phi_{KL}^{CD} \rangle c_{KL}^{CD} = f_{KC} (2c_{KI}^{CA} - c_{KI}^{AC}) - L_{KLCI} c_{KL}^{CA} + L_{KACD} c_{KI}^{CD} \tag{8}$$

and

$$\begin{aligned}
\langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_K^C \rangle c_K^C &= P_{IJ}^{AB} \langle AB|IC \rangle c_J^C - P_{IJ}^{AB} \langle KB|IJ \rangle c_K^A \\
&- P_{IJ}^{AB} f_{IC} t_{II}^{AA} c_J^C \delta_{AB} - P_{IJ}^{AB} f_{KA} t_{II}^{AA} c_K^B \delta_{AB} \\
&- P_{IJ}^{AB} L_{KJCI} t_{JL}^{AA} c_K^C \delta_{AB} + P_{IJ}^{AB} L_{KACB} t_{JJ}^{BB} c_K^C \delta_{IJ} \\
&- P_{IJ}^{AB} \langle JL|BI \rangle t_{JJ}^{BB} c_L^A + P_{IJ}^{AB} \langle IL|JB \rangle t_{II}^{BB} c_L^A \\
&+ P_{IJ}^{AB} \langle JA|BD \rangle t_{JJ}^{BB} c_I^D - P_{IJ}^{AB} \langle BJ|AD \rangle t_{JJ}^{AA} c_I^D \\
&- \langle KB|CC \rangle t_{II}^{CC} c_K^A \delta_{IJ} + \langle KK|CJ \rangle t_{KK}^{AA} c_I^C \delta_{AB} \tag{9}
\end{aligned}$$

Combining all elements above, the σ vector of pCCD-CISD is determined as follows

$$\text{pCCD-CISD } \sigma_0 = \langle \Phi_0 | \mathcal{H} | \Phi_K^C \rangle c_K^C + \langle \Phi_0 | \mathcal{H} | \Phi_{KL}^{CD} \rangle c_{KL}^{CD} \tag{10}$$

$$\text{pCCD-CISD } \sigma_I^A = \langle \Phi_I^A | \mathcal{H} | \Phi_0 \rangle c_0 + \langle \Phi_I^A | \mathcal{H} | \Phi_K^C \rangle c_K^C + \langle \Phi_I^A | \mathcal{H} | \Phi_{KL}^{CD} \rangle c_{KL}^{CD} \tag{11}$$

$$\text{pCCD-CISD } \sigma_{IJ}^{AB} = \langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_0 \rangle c_0 + \langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_K^C \rangle c_K^C + \langle \Phi_{IJ}^{AB} | \mathcal{H} | \Phi_{KL}^{CD} \rangle c_{KL}^{CD} \tag{12}$$

S1.4 A consistency analysis of pCCD-CI-based methods

The hydrogen molecule is a basic test system to quickly verify the correctness and consistency of the implemented CI corrections. Due to its size and simple electronic structure comprising only two electrons, H_2 serves as an inexpensive reference system and allows us to probe whether a dynamical energy correction on top of pCCD gives physically meaningful results. For instance, selected perturbation theory corrections on top of pCCD yield non-zero correlation energies when applied to the H_2 molecule, which obviously should not happen as orbital-optimized (OO-)pCCD is exact for any two-electron system. Table S1 summarizes the energy differences of various CI and LCC corrections with respect to the OO-pCCD reference values for various interatomic distances. All investigated post-pCCD methods provide a negligible energy correction, which confirms that the developed CI corrections (with and without electron-pair excitations) yield physically meaningful results. We should note that these differences are much smaller than the threshold for convergence (energy and residual vector) used during the diagonalization procedure of the CI optimization ($\leq 1E-5$).

TableS1: Total energy of the H_2 molecule obtained by OO-pCCD and the differences in total energies (ΔE) for various post-pCCD methods with respect to OO-pCCD. Note that pCCD-CISD' and pCCD-CISD are abbreviated by CISD' and CISD, respectively.

r_{H-H} [Å]	OO-pCCD	$\Delta E [E_h]$			
		CISD'	CISD	fpLCCSD	fpCCSD
0.400	-0.976798	-4.2E-09	-1.6E-07	1.6E-07	-1.6E-07
0.600	-1.153518	-2.5E-09	5.6E-08	-5.8E-08	5.8E-08
0.800	-1.170406	4.5E-09	2.0E-07	-2.0E-07	2.0E-07
1.000	-1.145759	0.0E+00	-5.2E-07	5.2E-07	-5.2E-07
1.200	-1.112068	-8.5E-10	-1.5E-06	1.5E-06	-1.5E-06
1.400	-1.080138	-6.1E-09	-1.9E-06	1.9E-06	-1.9E-06

S2 Doubles correction for the N₂ molecule

distance [Å]	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
0.700	-108.10063	-108.10428	-108.10300	-108.10643	-108.11348	-108.11013	-108.10771
0.800	-108.84659	-108.85078	-108.85017	-108.85405	-108.86210	-108.85818	-108.85425
0.900	-109.19790	-109.20283	-109.20336	-109.20778	-109.21705	-109.21247	-109.20613
1.000	-109.33838	-109.34432	-109.34622	-109.35125	-109.36195	-109.35661	-109.34713
1.100	-109.36798	-109.37535	-109.37872	-109.38447	-109.39673	-109.39054	-109.37711
1.200	-109.34164	-109.35103	-109.35611	-109.36267	-109.37662	-109.36948	-109.35092
1.300	-109.28984	-109.30207	-109.30888	-109.31636	-109.33203	-109.32380	-109.29890
1.400	-109.22937	-109.24540	-109.25394	-109.26247	-109.27987	-109.27032	-109.23767
1.500	-109.16919	-109.18994	-109.20050	-109.21025	-109.22953	-109.21818	-109.17606
1.600	-109.11371	-109.13998	-109.15273	-109.16419	-109.18691	-109.17282	-109.11850
1.800	-109.02197	-109.05764	-109.07838	-109.09326	-109.12443	-109.10119	-109.02311
2.000	-108.95762	-108.99855	-109.02822	-109.04850	-109.10477	-109.06071	-108.96092
2.200	-108.91890	-108.96283	-108.99615	-109.02353	-109.14949	-109.04897	-108.77844
2.400	-108.89934	-108.94761	-108.97686	-109.01224	-109.36776	-109.05665	-108.77609
2.800	-108.88613	-108.94739	-108.95962	-109.00969	-107.53280		-108.78867
3.200	-108.88310	-108.95563	-108.95475	-109.01476	-108.31235	-109.09946	-108.77690

Table S2: Total electronic energies [E_h] for the ground state of N₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

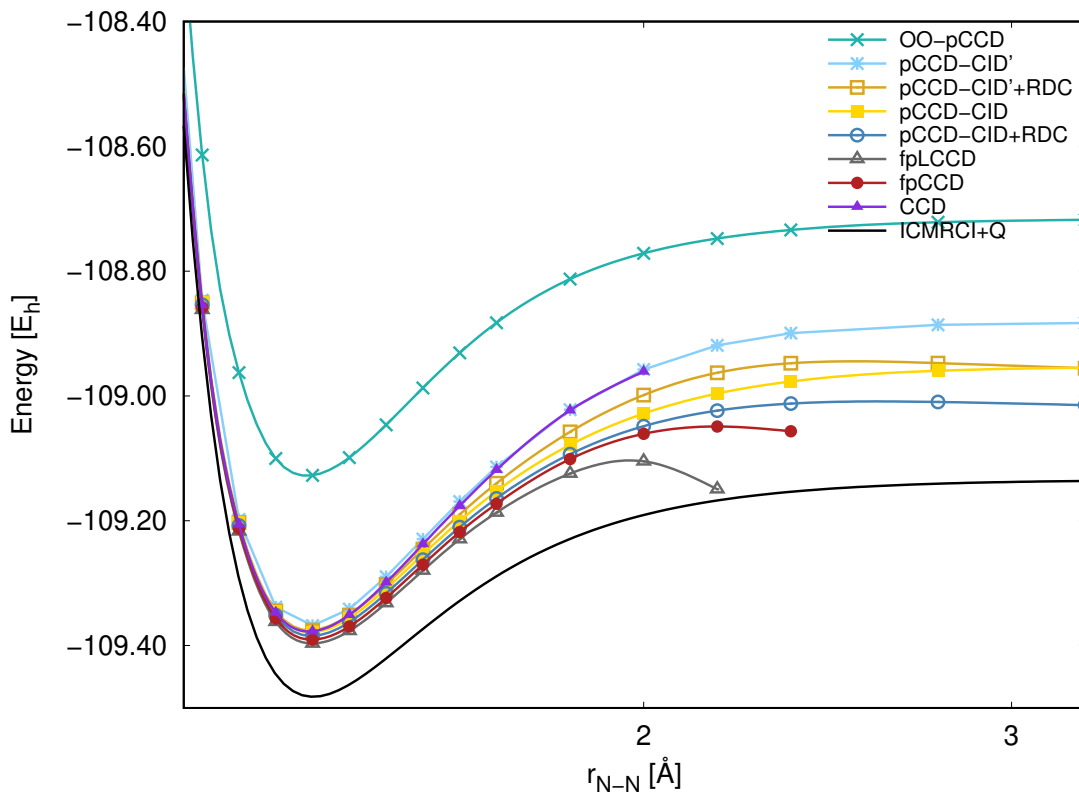


Figure S1: Potential energy surfaces of the ground states of N₂ determined for various post-pCCD with double excitations. The superscript ' indicates that the CI operator also includes the electron pair sector. RDC: renormalized Davidson correction. The ICMRCI+Q potential energy surface is approximated by a Morse potential exploiting the spectroscopic constants presented in ref. 1 and should be considered as a guide for the eye.

S3 Singles and Doubles correction for the N₂ molecule

distance [Å]	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD
0.700	-108.10131	-108.10501	-108.10391	-108.10740	-108.11457	-108.11109	-108.10870
0.800	-108.84738	-108.85164	-108.85094	-108.85490	-108.86309	-108.85898	-108.85560
0.900	-109.19889	-109.20390	-109.20426	-109.20879	-109.21826	-109.21338	-109.20807
1.000	-109.33960	-109.34565	-109.34732	-109.35253	-109.36349	-109.35769	-109.34988
1.100	-109.36948	-109.37700	-109.38005	-109.38605	-109.39870	-109.39177	-109.38094
1.200	-109.34343	-109.35304	-109.35765	-109.36457	-109.37906	-109.37082	-109.35608
1.300	-109.29190	-109.30443	-109.31058	-109.31855	-109.33489	-109.32514	-109.30561
1.400	-109.23163	-109.24802	-109.25565	-109.26480	-109.28297	-109.27145	-109.24608
1.500	-109.17136	-109.19254	-109.20188	-109.21234	-109.23230	-109.21866	-109.18626
1.600	-109.11553	-109.14200	-109.15366	-109.16562	-109.18775	-109.17136	-109.13054
1.800	-109.02295	-109.05906	-109.07775	-109.09357	-109.12440	-109.09869	-109.03900
2.000	-108.95805	-108.99939	-109.02627	-109.04776	-109.10328	-109.05692	-108.98135
2.200	-108.91896	-108.96331	-108.99293	-109.02188	-109.14809	-109.04497	-108.79020
2.400	-108.89924	-108.94816	-108.97254	-109.00992	-109.38298	-109.05329	-108.78914
2.800	-108.88591	-108.94857	-108.95394	-109.00676	-107.81148	not converge	-108.80282
3.200	-108.88277	-108.95726	-108.94935	-109.01235	-108.37501	not converge	-108.79339

Table S3: Total electronic energies [E_h] for the ground state of N₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

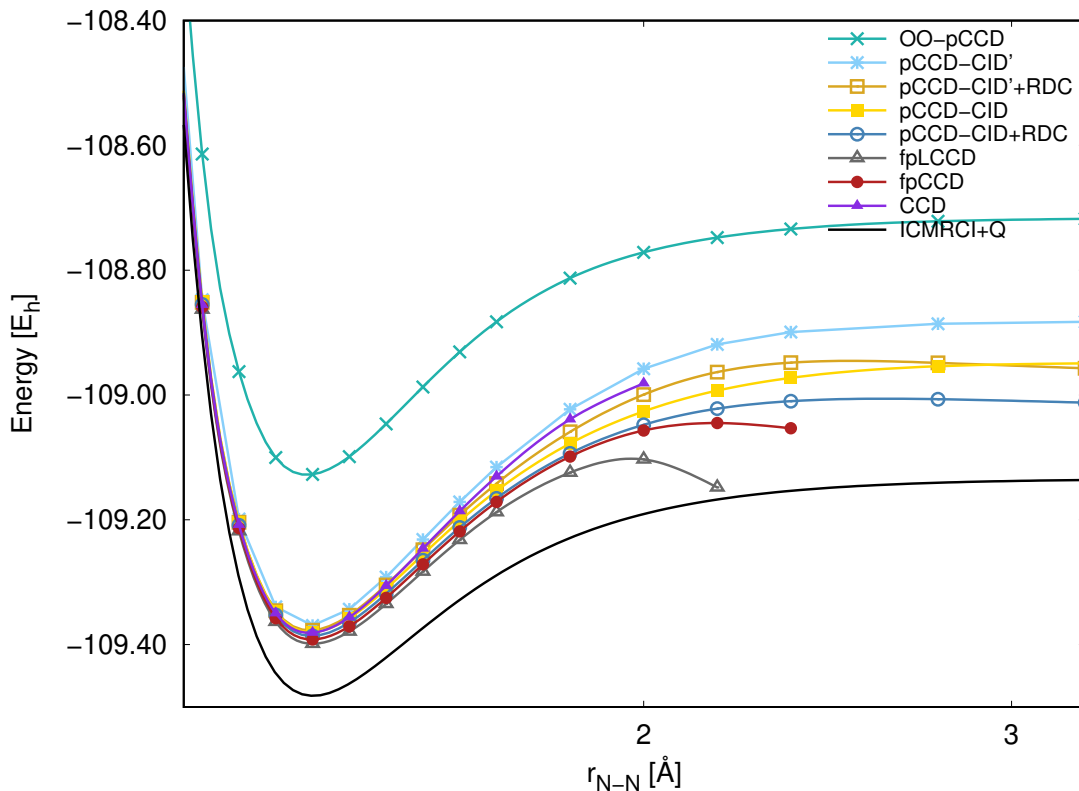


Figure S2: Potential energy surfaces of the ground states of N₂ determined for various post-pCCD with single and double excitations. The superscript ' indicates that the CI operator also includes the electron pair sector. RDC: renormalized Davidson correction. The ICMRCI+Q potential energy surface is approximated by a Morse potential exploiting the spectroscopic constants presented in ref. 1 and should be considered as a guide for the eye.

S4 Doubles correction for the F₂ molecule

distance [Å]	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
1.200	-199.26460	-199.27187	-199.27219	-199.27898	-199.29366	-199.28886	-199.27910
1.300	-199.29567	-199.30347	-199.30638	-199.31337	-199.32868	-199.32360	-199.30928
1.400	-199.30293	-199.31136	-199.31708	-199.32418	-199.33985	-199.33461	-199.31501
1.500	-199.29774	-199.30687	-199.31558	-199.32258	-199.33849	-199.33318	-199.30762
1.600	-199.28684	-199.29673	-199.30852	-199.31564	-199.33130	-199.32601	-199.29392
1.700	-199.27415	-199.28478	-199.29951	-199.30658	-199.32192	-199.31673	-199.27793
1.800	-199.26178	-199.27308	-199.29058	-199.29759	-199.31250	-199.30745	-199.26194
1.900	-199.25078	-199.26260	-199.28261	-199.28954	-199.30395	-199.29907	-199.24718
2.000	-199.24153	-199.25371	-199.27588	-199.28275	-199.29663	-199.29192	-199.23424
2.100	-199.23403	-199.24641	-199.27047	-199.27729	-199.29066	-199.28612	-199.22329
2.200	-199.22810	-199.24055	-199.26620	-199.27297	-199.28588	-199.28149	-199.21426
2.300	-199.22346	-199.23590	-199.26284	-199.26959	-199.28207	-199.27781	-199.20694
2.400	-199.21986	-199.23222	-199.26022	-199.26694	-199.27906	-199.27491	-199.20108
2.500	-199.21707	-199.22931	-199.25816	-199.26487	-199.27667	-199.27261	-199.19645
2.600	-199.21488	-199.22700	-199.25654	-199.26324	-199.27477	-199.27079	-199.19281
2.700	-199.21317	-199.22515	-199.25526	-199.26195	-199.27325	-199.26934	-199.18998
2.800	-199.21182	-199.22368	-199.25424	-199.26093	-199.27205	-199.26819	-199.18781
2.900	-199.21075	-199.22248	-199.25344	-199.26012	-199.27108	-199.26727	-199.18616
3.000	-199.20989	-199.22152	-199.25280	-199.25948	-199.27031	-199.26653	-199.18493
3.500	-199.20750	-199.21867	-199.25104	-199.25772	-199.26815	-199.26447	-199.18244
4.000	-199.20646	-199.21733	-199.25036	-199.25702	-199.26729	-199.26365	

Table S4: Total electronic energies [E_h] for the ground state of F₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

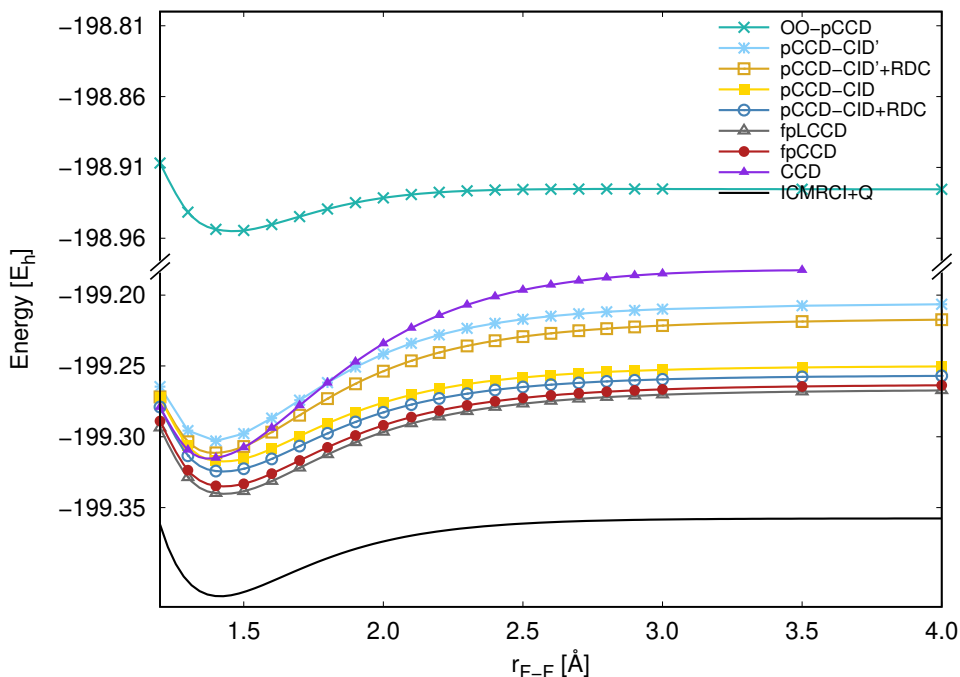


Figure S3: Potential energy surfaces of the ground states of F₂ determined for various post-pCCD with double excitations. The superscript ' indicates that the CI operator also includes the electron pair sector. RDC: renormalized Davidson correction. The ICMRCI+Q potential energy surface is approximated by a Morse potential exploiting the spectroscopic constants presented in ref. 1 and should be considered as a guide for the eye.

S5 Singles and Doubles correction for the F₂ molecule

distance [Å]	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD
1.200	-199.26595	-199.27343	-199.27313	-199.28019	-199.29527	-199.28985	-199.28255
1.300	-199.29699	-199.30502	-199.30722	-199.31450	-199.33020	-199.32447	-199.31367
1.400	-199.30420	-199.31285	-199.31777	-199.32515	-199.34119	-199.33528	-199.32052
1.500	-199.29893	-199.30828	-199.31608	-199.32349	-199.33957	-199.33362	-199.31441
1.600	-199.28796	-199.29808	-199.30884	-199.31621	-199.33208	-199.32622	-199.30215
1.700	-199.27521	-199.28610	-199.29968	-199.30696	-199.32242	-199.31674	-199.28774
1.800	-199.26282	-199.27442	-199.29064	-199.29783	-199.31277	-199.30731	-199.27345
1.900	-199.25182	-199.26399	-199.28260	-199.28969	-199.30406	-199.29883	-199.26045
2.000	-199.24259	-199.25516	-199.27582	-199.28283	-199.29664	-199.29163	-199.24927
2.100	-199.23510	-199.24791	-199.27039	-199.27732	-199.29061	-199.28581	-199.24002
2.200	-199.22917	-199.24208	-199.26609	-199.27297	-199.28579	-199.28117	-199.23258
2.300	-199.22453	-199.23742	-199.26271	-199.26956	-199.28196	-199.27749	-199.22668
2.400	-199.22092	-199.23373	-199.26006	-199.26688	-199.27893	-199.27458	-199.22207
2.500	-199.21810	-199.23078	-199.25799	-199.26478	-199.27653	-199.27228	-199.21848
2.600	-199.21588	-199.22842	-199.25635	-199.26313	-199.27462	-199.27046	-199.21569
2.700	-199.21414	-199.22653	-199.25505	-199.26182	-199.27310	-199.26901	-199.21352
2.800	-199.21276	-199.22500	-199.25402	-199.26079	-199.27189	-199.26785	-199.21183
2.900	-199.21167	-199.22376	-199.25320	-199.25997	-199.27092	-199.26693	-199.21052
3.000	-199.21079	-199.22275	-199.25255	-199.25932	-199.27015	-199.26619	-199.20950
3.500	-199.20830	-199.21974	-199.25078	-199.25754	-199.26800	-199.26413	-199.20687
4.000	-199.20721	-199.21831	-199.25009	-199.25684	-199.26715	-199.26332	

Table S5: Total electronic energies [E_h] for the ground state of F₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

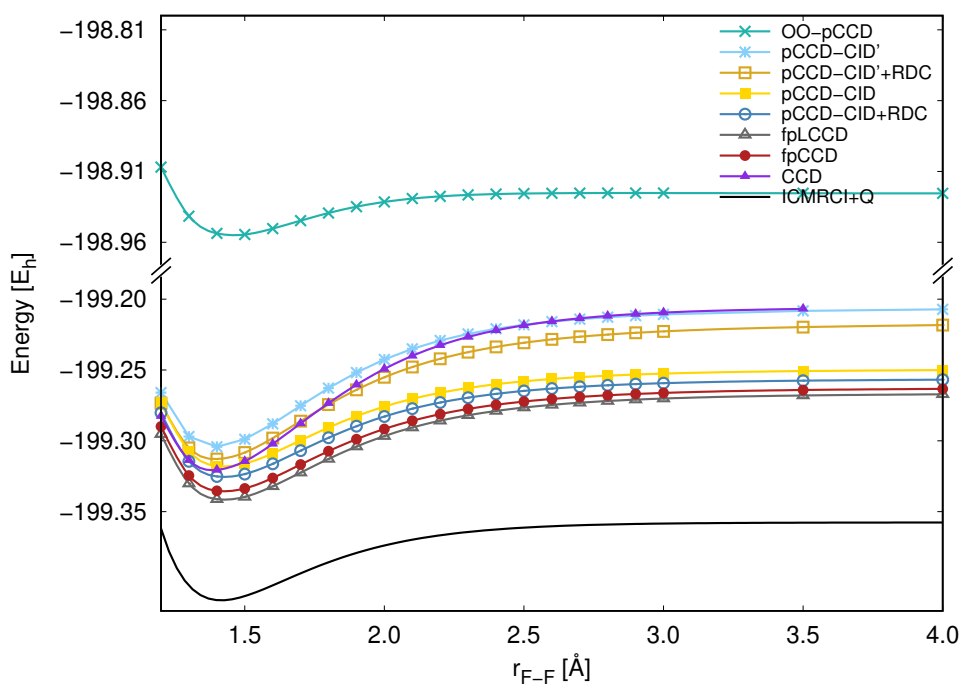


Figure S4: Potential energy surfaces of the ground states of F₂ determined for various post-pCCD with single and double excitations. The superscript ' indicates that the CI operator also includes the electron pair sector. RDC: renormalized Davidson correction. The ICMRCI+Q potential energy surface is approximated by a Morse potential exploiting the spectroscopic constants presented in ref. 1 and should be considered as a guide for the eye.

S6 Doubles correction for ThO

distance	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
1.800	-26539.60582	-26539.61764	-26539.61397	-26539.62465	-26539.65022	-26539.64299	-26539.63269
1.820	-26539.60726	-26539.61917	-26539.61553	-26539.62625	-26539.65193	-26539.64466	-26539.63417
1.840	-26539.60796	-26539.61995	-26539.61635	-26539.62712	-26539.65291	-26539.64566	-26539.63490
1.860	-26539.60798	-26539.62005	-26539.61646	-26539.62728	-26539.65313	-26539.64588	-26539.63495
1.880	-26539.60736	-26539.61952	-26539.61597	-26539.62683	-26539.65288	-26539.64543	-26539.63437
1.900	-26539.60617	-26539.61842	-26539.61499	-26539.62581	-26539.65189	-26539.64448	-26539.63321
1.920	-26539.60446	-26539.61688	-26539.61331	-26539.62427	-26539.65046	-26539.64301	-26539.63152
1.940	-26539.60225	-26539.61469	-26539.61123	-26539.62224	-26539.64855	-26539.64105	-26539.62934
1.960	-26539.59961	-26539.61214	-26539.60872	-26539.61977	-26539.64622	-26539.63866	-26539.62672
1.980	-26539.59656	-26539.60919	-26539.60588	-26539.61699	-26539.64345	-26539.63586	-26539.62370

Table S6: Total electronic energies [E_h] for the ground state of ThO obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

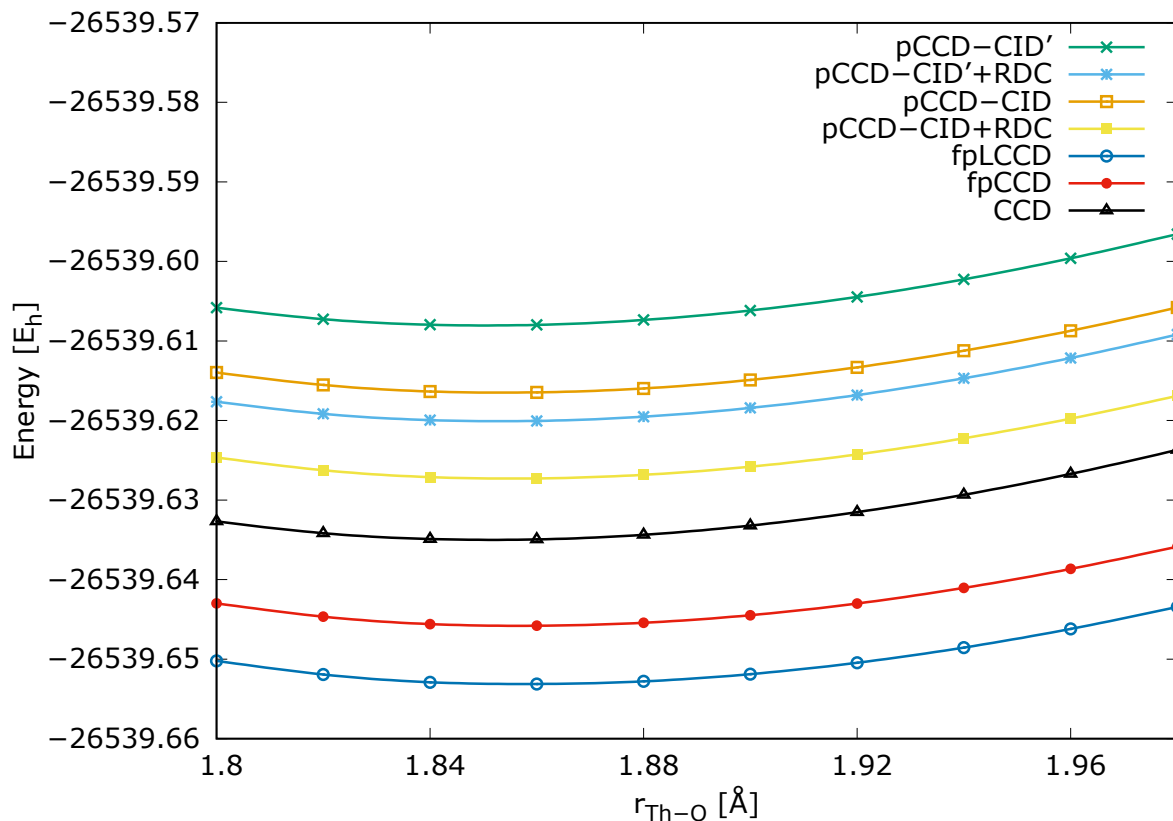


Figure S5: Potential energy surfaces of the ground state of ThO determined for various post-pCCD and conventional CC methods featuring only double excitations.

S7 Singles and Doubles correction for ThO

distance [\AA]	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD	CCSD(T)
1.800	-26539.60946	-26539.62257	-26539.61741	-26539.62939	-26539.66004	-26539.64807	-26539.63886	-26539.663433
1.820	-26539.61095	-26539.62416	-26539.61900	-26539.63106	-26539.66197	-26539.64974	-26539.64046	-26539.665364
1.840	-26539.61169	-26539.62501	-26539.61985	-26539.63200	-26539.66317	-26539.65068	-26539.64131	-26539.666562
1.860	-26539.61174	-26539.62518	-26539.61999	-26539.63222	-26539.66361	-26539.65087	-26539.64149	-26539.667086
1.880	-26539.61117	-26539.62473	-26539.61953	-26539.63185	-26539.66354	-26539.65050	-26539.64104	-26539.666995
1.900	-26539.61002	-26539.62370	-26539.61850	-26539.63090	-26539.66290	-26539.64955	-26539.64001	-26539.666340
1.920	-26539.60835	-26539.62215	-26539.61694	-26539.62943	-26539.66176	-26539.64807	-26539.63845	-26539.665168
1.940	-26539.60619	-26539.62011	-26539.61489	-26539.62748	-26539.66016	-26539.64611	-26539.63641	-26539.663525
1.960	-26539.60359	-26539.61764	-26539.61241	-26539.62509	-26539.65893	-26539.64371	-26539.63393	-26539.661451
1.980	-26539.60058	-26539.61477	-26539.60954	-26539.62231	-26539.65661	-26539.64090	-26539.63104	-26539.658986

Table S7: Total electronic energies [E_h] for the ground state of ThO obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

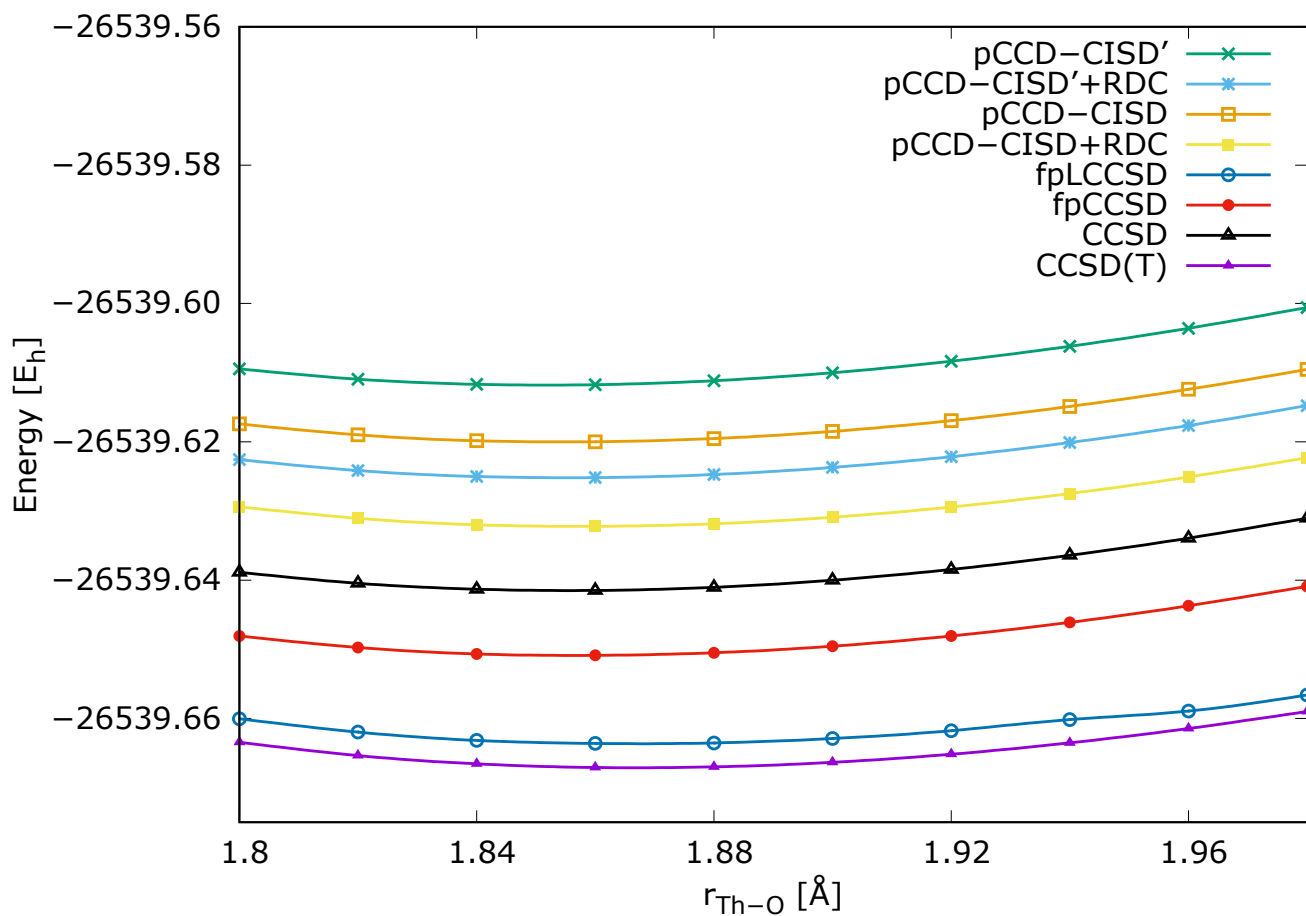


Figure S6: Potential energy surfaces of the ground state of ThS determined for various post-pCCD and conventional CC methods featuring only double excitations..

S8 Doubles correction for ThS

distance	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
1.750	-26862.66992	-26862.68264	-26862.67498	-26862.68672	-26862.71564	-26862.70666	-26862.70222
1.850	-26862.83131	-26862.84378	-26862.83626	-26862.84776	-26862.87602	-26862.86723	-26862.86281
1.950	-26862.93829	-26862.95058	-26862.94323	-26862.95457	-26862.98234	-26862.97367	-26862.96914
2.050	-26863.00658	-26863.01876	-26863.01162	-26863.02284	-26863.05027	-26863.04166	-26863.03695
2.150	-26863.04865	-26863.06056	-26863.05381	-26863.06521	-26863.09266	-26863.08406	-26863.07724
2.250	-26863.06975	-26863.08165	-26863.07504	-26863.08641	-26863.11374	-26863.10511	-26863.09787
2.350	-26863.07679	-26863.08874	-26863.0822	-26863.09359	-26863.12094	-26863.11222	-26863.10454
2.450	-26863.07400	-26863.08607	-26863.07953	-26863.09099	-26863.11846	-26863.10961	-26863.10143
2.550	-26863.06445	-26863.07671	-26863.07016	-26863.08171	-26863.10944	-26863.10041	-26863.0916
2.650	-26863.05041	-26863.06291	-26863.05628	-26863.06796	-26863.09601	-26863.08678	-26863.07733
2.750	-26863.03353	-26863.04632	-26863.03958	-26863.05141	-26863.07987	-26863.07039	-26863.06026
2.850	-26863.01505	-26863.02816	-26863.02129	-26863.0333	-26863.06224	-26863.05249	-26863.04161

TableS8: Total electronic energies [E_h] of ThS obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

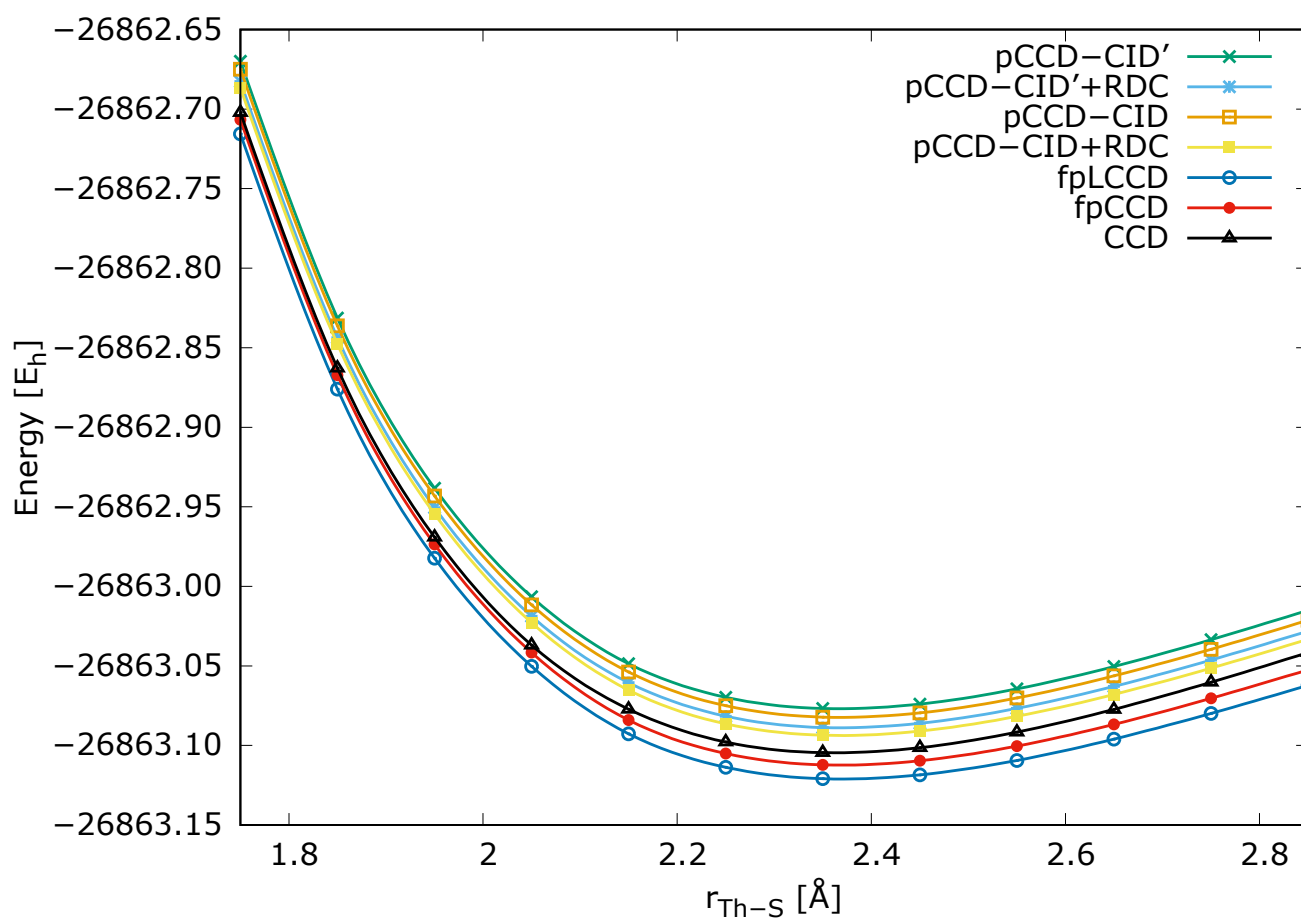


Figure S7: Potential energy surfaces of the ground state of ThO determined for various post-pCCD and conventional CC methods featuring double excitations.

S9 Singles and Doubles correction for ThS

distance	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD	CCSD(T)
1.750	-26862.672970	-26862.686855	-26862.6781356	-26862.6908552	-26862.725676	-26862.712834	-26862.70630	-26862.73123
1.850	-26862.834382	-26862.848026	-26862.8394289	-26862.8519238	-26862.886032	-26862.873335	-26862.86695	-26862.89161
1.950	-26862.941409	-26862.954898	-26862.9464422	-26862.9588025	-26862.99249	-26862.979726	-26862.97340	-26862.99801
2.050	-26863.009802	-26863.023226	-26863.0149017	-26863.0272043	-26863.060838	-26863.047763	-26863.04138	-26863.06614
2.150	-26863.051801	-26863.064940	-26863.0570126	-26863.0695395	-26863.103037	-26863.089751	-26863.08189	-26863.10699
2.250	-26863.073037	-26863.086250	-26863.0783545	-26863.0909504	-26863.124914	-26863.110872	-26863.1028	-26863.12843
2.350	-26863.080226	-26863.093596	-26863.0856517	-26863.0983843	-26863.13321	-26863.118075	-26863.10979	-26863.13618
2.450	-26863.077571	-26863.091181	-26863.0831353	-26863.0960694	-26863.132208	-26863.115542	-26863.10706	-26863.13441
2.550	-26863.068173	-26863.082109	-26863.0738867	-26863.0870797	-26863.125115	-26863.106401	-26863.09767	-26863.12623
2.650	-26863.054301	-26863.068643	-26863.0601735	-26863.0736842	-26863.114470	-26863.092821	-26863.08389	-26863.11390
2.750	-26863.03762	-26863.05244	-26863.0436580	-26863.0575455	-26863.10261	-26863.07646	-26863.06735	-26863.09911
2.850	-26863.01935	-26863.03472	-26863.0255747	-26863.0398936	-26863.09484	-26863.05853	-26863.04926	-26863.08306

TableS9: Total electronic energies [E_h] of ThS obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

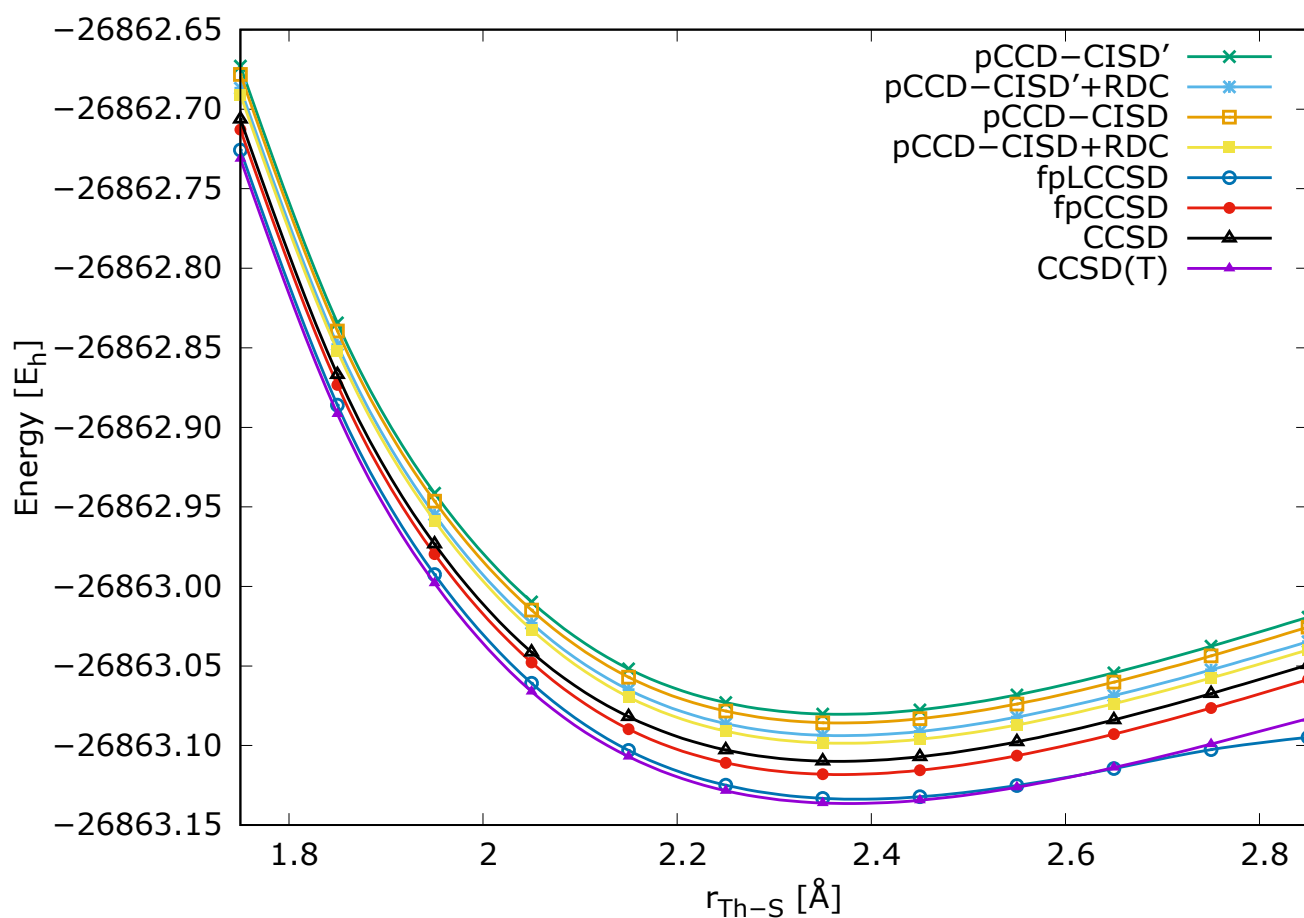


Figure S8: Potential energy surfaces of the ground state of ThS determined for various post-pCCD and conventional CC methods featuring single and double excitations.

S10 Doubles correction for UO_2^{2+}

distance	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
1.600	-28149.26303	-28149.28600	-28149.27444	-28149.29559	-28149.34846	-28149.33781	-28149.31910
1.625	-28149.27387	-28149.29742	-28149.28581	-28149.30735	-28149.36141	-28149.35045	-28149.33085
1.650	-28149.28026	-28149.30439	-28149.29280	-28149.31474	-28149.37003	-28149.35875	-28149.33766
1.675	-28149.28276	-28149.30751	-28149.29592	-28149.31827	-28149.37481	-28149.36320	-28149.34052
1.700	-28149.28191	-28149.30729	-28149.29583	-28149.31859	-28149.37650	-28149.36454	-28149.33993
1.725	-28149.27815	-28149.30421	-28149.29296	-28149.31614	-28149.37530	-28149.36298	-28149.33632
1.750	-28149.27186	-28149.29862	-28149.28757	-28149.31117	-28149.37166	-28149.35899	-28149.33006
1.775	-28149.26339	-28149.29088	-28149.28006	-28149.30407	-28149.36592	-28149.35287	-28149.32147
1.800	-28149.25302	-28149.28128	-28149.27071	-28149.29513	-28149.35834	-28149.34491	-28149.31083
1.825	-28149.24101	-28149.27006	-28149.25975	-28149.28457	-28149.34914	-28149.33534	-28149.29837
1.850	-28149.22758	-28149.25746	-28149.24739	-28149.27261	-28149.33854	-28149.32434	-28149.28427
1.875	-28149.21293	-28149.24366	-28149.23382	-28149.25943	-28149.32671	-28149.31213	-28149.26867

Table S10: Total electronic energies [E_h] of UO_2^{2+} obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

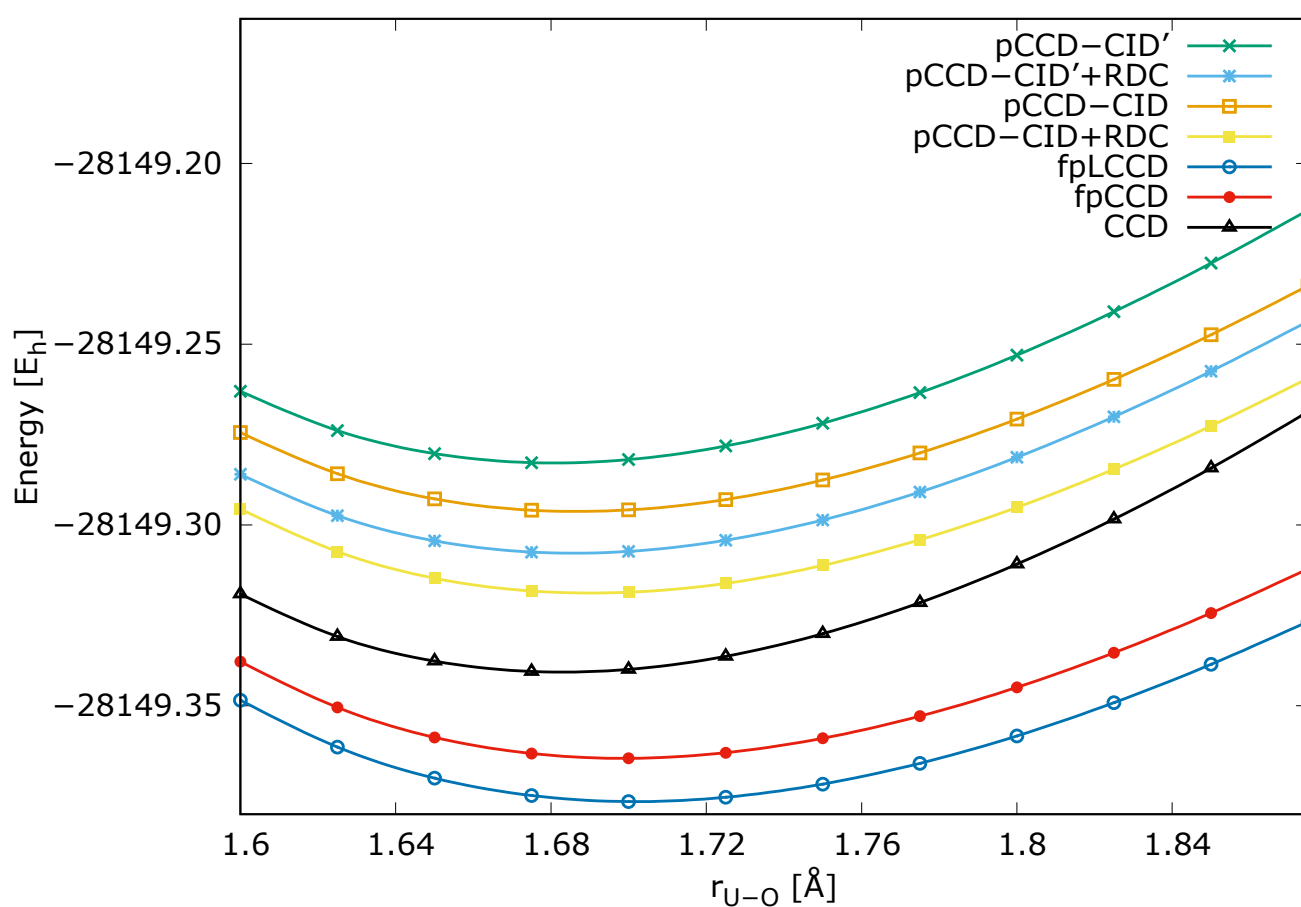


Figure S9: Potential energy surfaces of the ground state of UO_2^{2+} determined for various post-pCCD and conventional CC methods featuring double excitations.

S11 Singles and Doubles correction for UO_2^{2+}

distance	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD	CCSD(T)
1.600	-28149.26859	-28149.29361	-28149.27956	-28149.30312		-28149.34428	-28149.33209	-28149.36921
1.625	-28149.27967	-28149.30542	-28149.29115	-28149.31528	-28149.3779112	-28149.35702	-28149.34423	-28149.38304
1.650	-28149.28630	-28149.31280	-28149.29838	-28149.32310	-28149.3878198	-28149.36538	-28149.35189	-28149.39250
1.675	-28149.28906	-28149.31634	-28149.30174	-28149.32708	-28149.3939904	-28149.36984	-28149.35564	-28149.39816
1.700	-28149.28846	-28149.31656	-28149.30189	-28149.32785	-28149.3970895	-28149.37113	-28149.35599	-28149.40052
1.725	-28149.28495	-28149.31390	-28149.29924	-28149.32585	-28149.3975512	-28149.36946	-28149.35337	-28149.40003
1.750	-28149.27890	-28149.30875	-28149.29408	-28149.32134	-28149.3956306	-28149.36526	-28149.34816	-28149.39706
1.775	-28149.27067	-28149.30145	-28149.28679	-28149.31472	-28149.3917548	-28149.35886	-28149.34070	-28149.39193
1.800	-28149.26054	-28149.29230	-28149.27766	-28149.30627	-28149.3862424	-28149.35055	-28149.33129	-28149.38493
1.825	-28149.24878	-28149.28155	-28149.26694	-28149.29623	-28149.3793004	-28149.34054	-28149.32018	-28149.37633
1.850	-28149.23560	-28149.26944	-28149.25484	-28149.28482	-28149.3712623	-28149.32905	-28149.30762	-28149.36634
1.875	-28149.22122	-28149.25618	-28149.24155	-28149.27224	-28149.3623120	-28149.31628	-28149.29382	-28149.35516
1.900					-28149.3533285		-28149.27900	-28149.34298

Table S11: Total electronic energies [E_h] of UO_2^{2+} obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

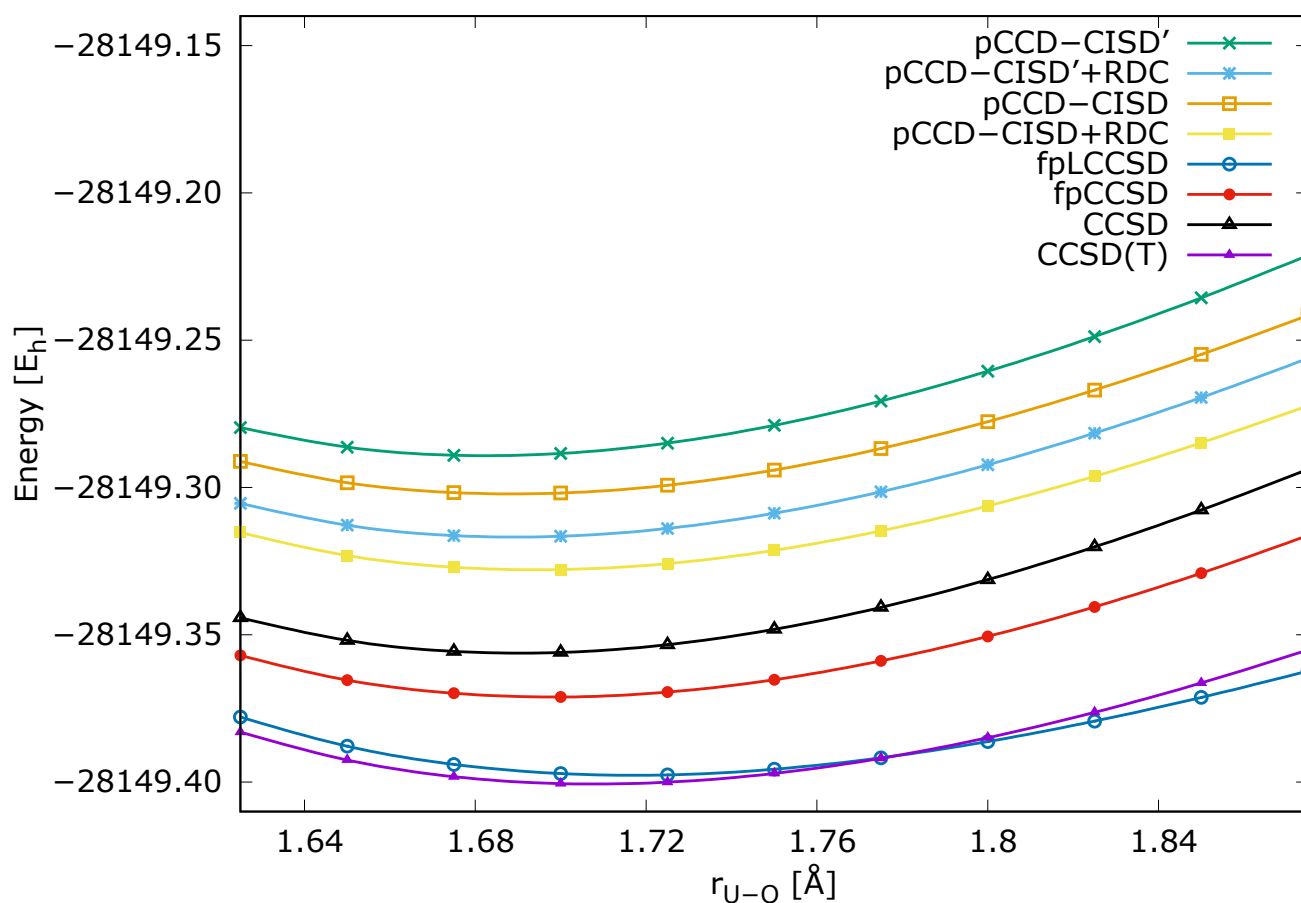


Figure S10: Potential energy surfaces of the ground state of UO_2^{2+} determined for various post-pCCD and conventional CC methods featuring single and double excitations.

S12 Doubles correction for UN₂

distance	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
1.650	-28108.97495	-28109.00086	-28108.98674	-28109.01090	-28109.07305	-28109.06034	-28109.04098
1.675	-28108.98259	-28109.00907	-28108.99465	-28109.01917	-28109.08243	-28109.06939	-28109.0492
1.700	-28108.98627	-28109.01347	-28108.99810	-28109.02296	-28109.08734	-28109.07391	-28109.05362
1.725	-28108.98691	-28109.01468	-28108.99915	-28109.02437	-28109.08994	-28109.07616	-28109.05469
1.750	-28108.98465	-28109.01301	-28108.99732	-28109.02293	-28109.08971	-28109.07556	-28109.05284
1.775	-28108.97987	-28109.00884	-28108.99301	-28109.01900	-28109.08700	-28109.07247	-28109.04841
1.800	-28108.97290	-28109.00251	-28108.98654	-28109.01293	-28109.08217	-28109.06725	-28109.04173
1.825	-28108.96405	-28108.99433	-28108.97825	-28109.00503	-28109.07552	-28109.06020	-28109.03308
1.850	-28108.95360	-28108.98459	-28108.96842	-28108.99559	-28109.06734	-28109.05161	-28109.02269
1.875	-28108.94179	-28108.97354	-28108.95731	-28108.98488	-28109.05789	-28109.04174	-28109.01078
1.900	-28108.92887	-28108.96142	-28108.94516	-28108.97314	-28109.04742	-28109.03084	-28108.99754

TableS12: Total electronic energies [E_h] of UN₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

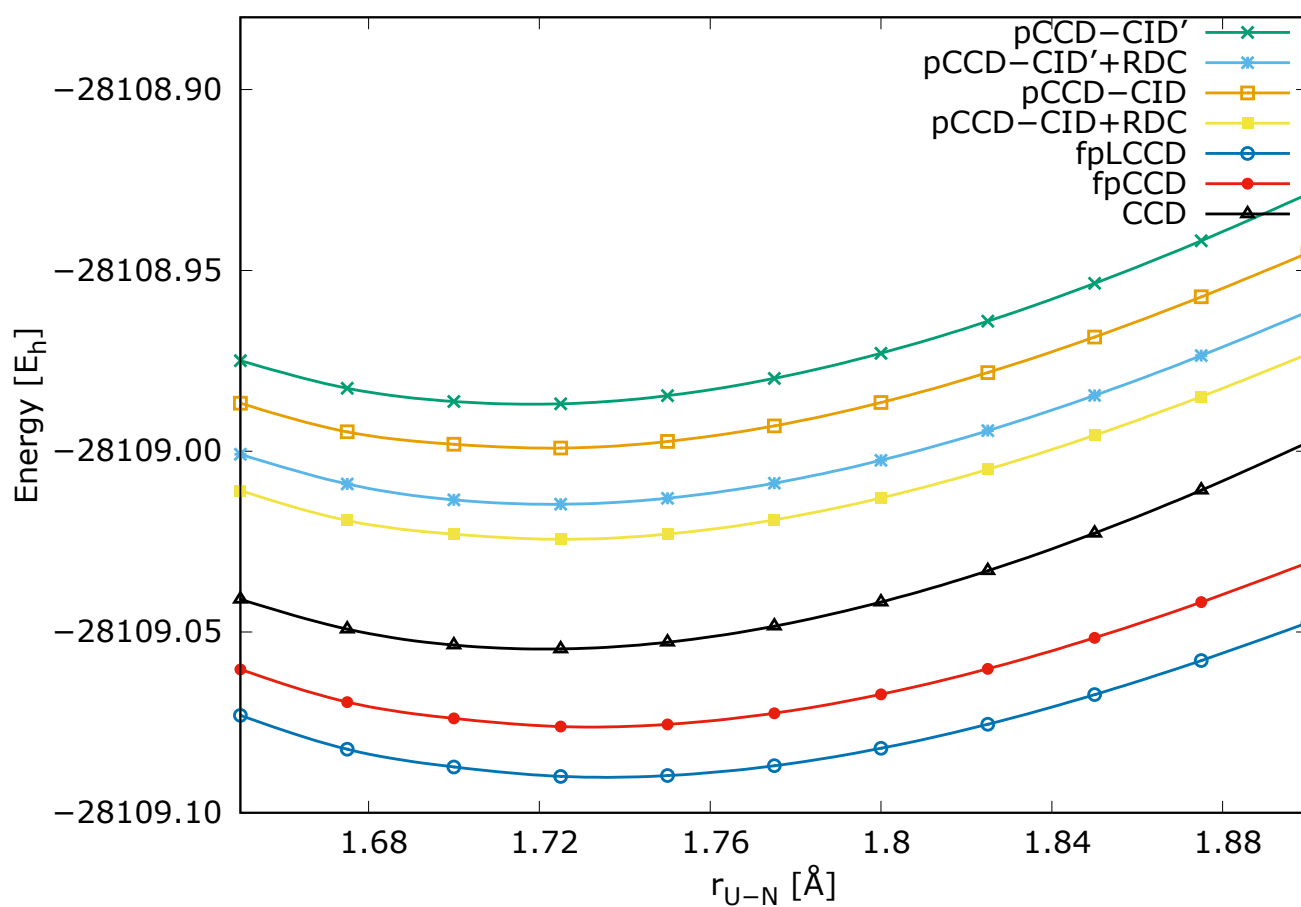


Figure S11: Potential energy surfaces of the ground state of UN₂ determined for various post-pCCD and conventional CC methods featuring double excitations.

S13 Singles and Doubles correction for UN₂

distance	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD	CCSD(T)
1.650	-28108.97972	-28109.00753	-28108.99122	-28109.01757	-28109.08992	-28109.06768	-28109.05393	-28109.09652
1.675	-28108.98749	-28109.01595	-28108.99924	-28109.02605	-28109.10019	-28109.07678	-28109.06409	-28109.10672
1.700	-28108.99124	-28109.02049	-28109.00276	-28109.03000	-28109.10594	-28109.08122	-28109.06787	-28109.11322
1.725	-28108.99203	-28109.02195	-28109.00395	-28109.03168	-28109.10970	-28109.08352	-28109.06964	-28109.11647
1.750	-28108.98993	-28109.02055	-28109.00229	-28109.03053	-28109.11075	-28109.08297	-28109.06851	-28109.11689
1.775	-28108.98530	-28109.01665	-28108.99813	-28109.02689	-28109.10949	-28109.07993	-28109.06483	-28109.11483
1.800	-28108.97850	-28109.01061	-28108.99183	-28109.02112	-28109.10622	-28109.07471	-28109.05895	-28109.11061
1.825	-28108.96981	-28109.00272	-28108.98371	-28109.01353	-28109.10131	-28109.06763	-28109.05113	-28109.10452
1.850	-28108.95952	-28108.99326	-28108.97403	-28109.00439	-28109.09496	-28109.05894	-28109.04163	-28109.09680
1.875	-28108.94785	-28108.98247	-28108.96306	-28108.99396	-28109.08739	-28109.04889	-28109.03068	-28109.08766
1.900	-28108.93504	-28108.97058	-28108.95102	-28108.98248	-28109.07869	-28109.03769	-28109.01848	-28109.07731

TableS13: Total electronic energies [E_h] of UN₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

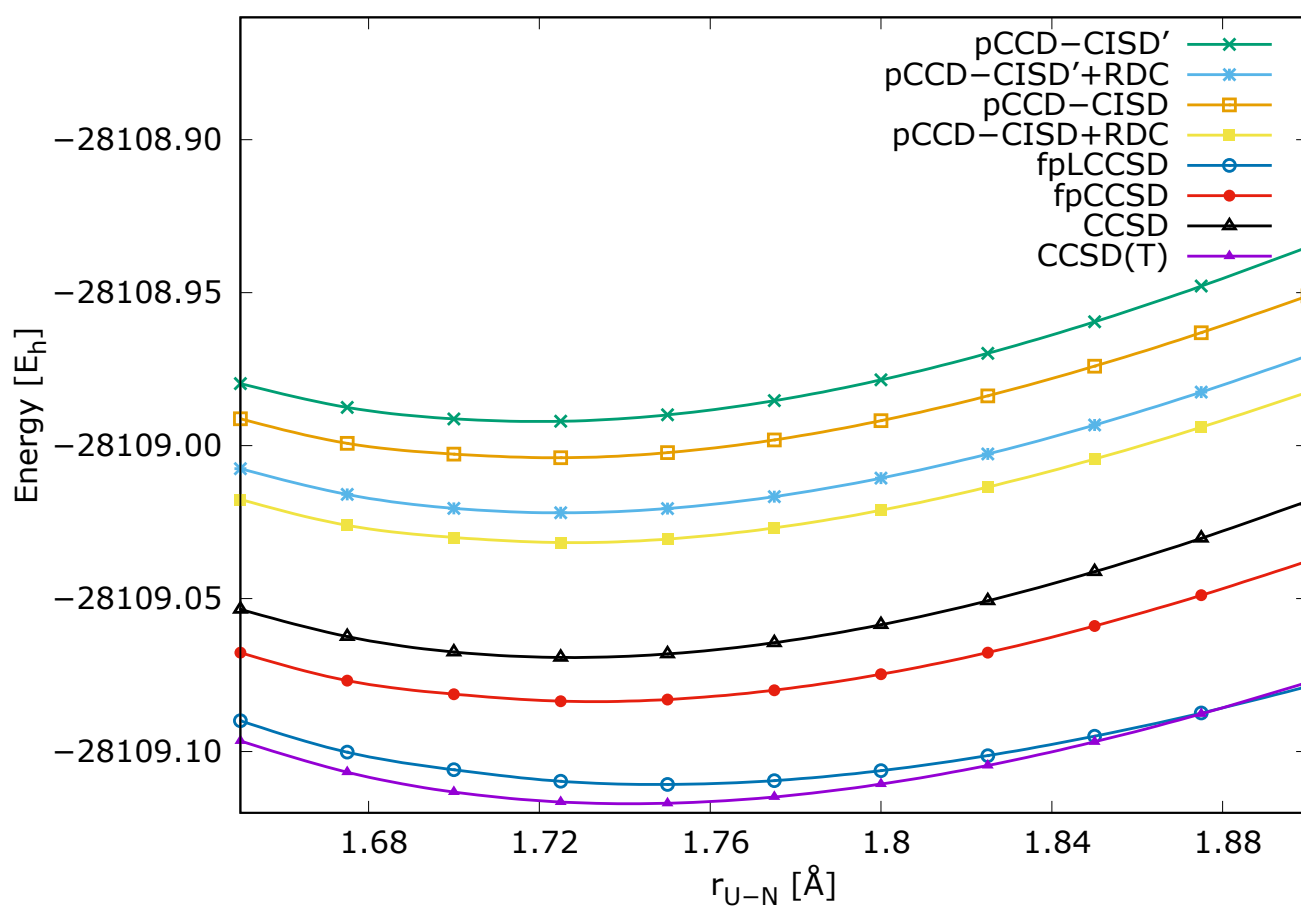


Figure S12: Potential energy surfaces of the ground state of UN₂ determined for various post-pCCD and conventional CC methods featuring single and double excitations.

S14 Doubles correction for PaO_2^+

distance	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
1.650	-27374.72112	-27374.74192	-27374.73089	-27374.75048	-27374.79867	-27374.78879	-27374.77453
1.675	-27374.73409	-27374.75520	-27374.74421	-27374.76402	-27374.81285	-27374.80281	-27374.78781
1.700	-27374.74324	-27374.76466	-27374.75374	-27374.77377	-27374.82326	-27374.81304	-27374.79724
1.725	-27374.74901	-27374.77073	-27374.75992	-27374.78017	-27374.83031	-27374.81992	-27374.80325
1.750	-27374.75177	-27374.77380	-27374.76307	-27374.78353	-27374.83432	-27374.82376	-27374.80623
1.775	-27374.75187	-27374.77422	-27374.76366	-27374.78433	-27374.83577	-27374.82505	-27374.80651
1.800	-27374.74961	-27374.77229	-27374.76191	-27374.78279	-27374.83489	-27374.82400	-27374.80438
1.825	-27374.74523	-27374.76825	-27374.75810	-27374.77918	-27374.83194	-27374.82088	-27374.80009
1.850	-27374.73898	-27374.76235	-27374.75244	-27374.77372	-27374.82715	-27374.81592	-27374.79388
1.875	-27374.73107	-27374.75479	-27374.74512	-27374.76659	-27374.82067	-27374.80928	-27374.78595
1.900	-27374.72167	-27374.74575	-27374.73634	-27374.75799	-27374.81273	-27374.80118	-27374.77648
1.925	-27374.71095	-27374.73541	-27374.72624	-27374.74807	-27374.80347	-27374.79175	-27374.76565
1.950	-27374.69904	-27374.72390	-27374.71498	-27374.73698	-27374.79304	-27374.78116	-27374.75359
1.975	-27374.68610	-27374.71137	-27374.70273	-27374.72492	-27374.78165	-27374.76961	-27374.74007
2.000	-27374.67223	-27374.69792	-27374.68952	-27374.71187	-27374.76926	-27374.75705	-27374.72639

TableS14: Total electronic energies $[E_h]$ of PaO_2^+ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

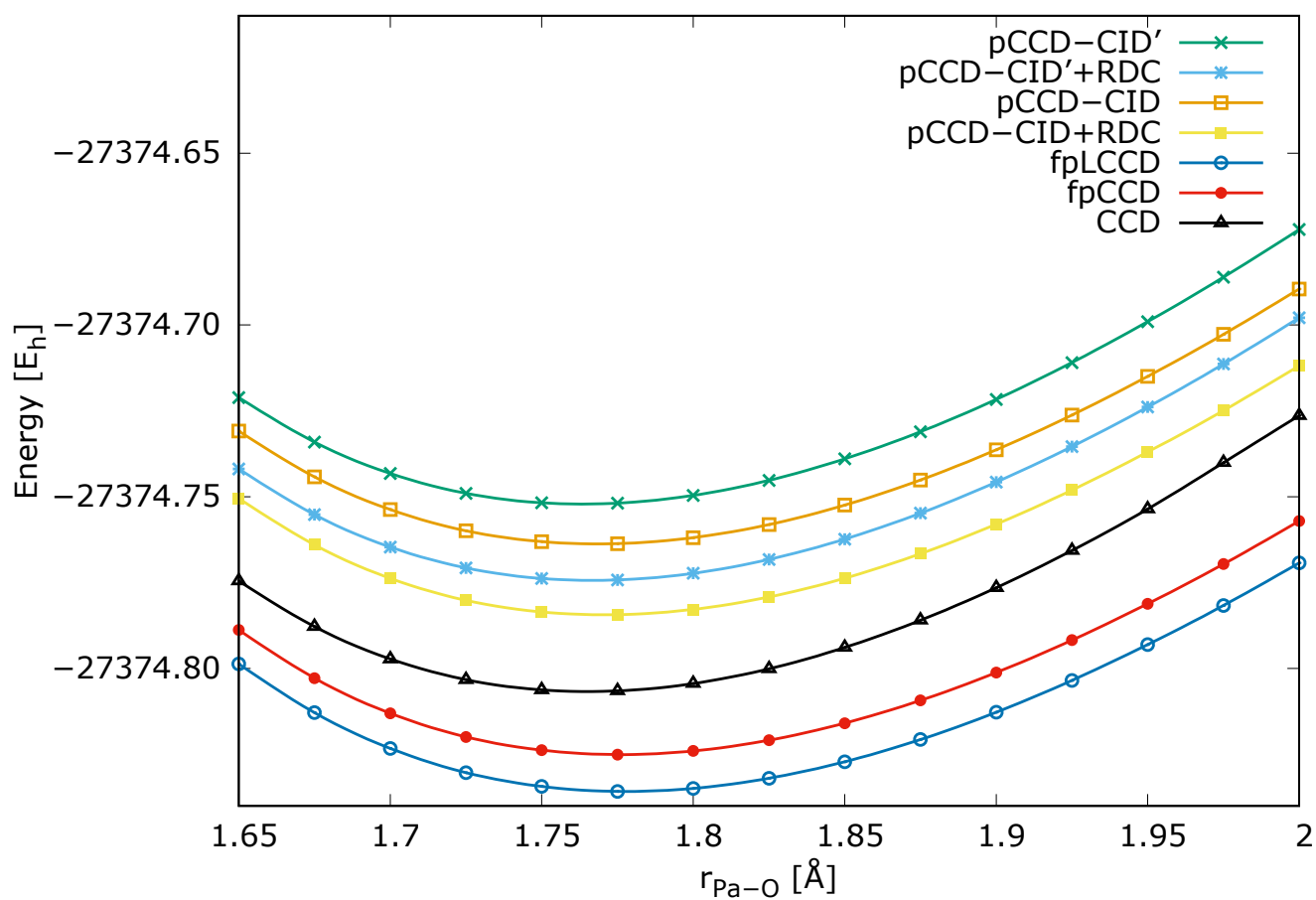


Figure S13: Potential energy surfaces of the ground state of PaO_2^+ determined for various post-pCCD and conventional CC methods featuring double excitations.

S15 Singles and Doubles correction for PaO₂⁺

distance	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD	CCSD(T)
1.650	-27374.72557	-27374.74796	-27374.73493	-27374.75633	-27374.81020	-27374.79427	-27374.78377	-27374.81556
1.675	-27374.73871	-27374.76150	-27374.74840	-27374.77014	-27374.82507	-27374.80839	-27374.79748	-27374.83028
1.700	-27374.74803	-27374.77124	-27374.75809	-27374.78017	-27374.83615	-27374.81872	-27374.80736	-27374.84123
1.725	-27374.75398	-27374.77761	-27374.76443	-27374.78686	-27374.84410	-27374.82570	-27374.81384	-27374.84886
1.750	-27374.75693	-27374.78099	-27374.76776	-27374.79053	-27374.84899	-27374.82961	-27374.8173	-27374.85353
1.775	-27374.75723	-27374.78174	-27374.76851	-27374.79165	-27374.85139	-27374.83095	-27374.81808	-27374.85559
1.800	-27374.75516	-27374.78013	-27374.76693	-27374.79044	-27374.85152	-27374.82992	-27374.81646	-27374.85533
1.825	-27374.75099	-27374.77644	-27374.76329	-27374.78717	-27374.84966	-27374.82680	-27374.81271	-27374.85299
1.850	-27374.74494	-27374.77088	-27374.75781	-27374.78207	-27374.84603	-27374.82179	-27374.80704	-27374.84882
1.875	-27374.73722	-27374.76367	-27374.75066	-27374.77529	-27374.84078	-27374.81505	-27374.79965	-27374.84301
1.900	-27374.72801	-27374.75498	-27374.74203	-27374.76705	-27374.83413	-27374.8068	-27374.79074	-27374.83575
1.925	-27374.71747	-27374.74498	-27374.73209	-27374.75750	-27374.82626	-27374.79717	-27374.78046	-27374.84827
1.950	-27374.70575	-27374.73382	-27374.72099	-27374.74679	-27374.81732	-27374.78633	-27374.76897	-27374.81751
1.975	-27374.69299	-27374.72165	-27374.70890	-27374.73511	-27374.80754	-27374.77447	-27374.75638	-27374.80682
2.000	-27374.67930	-27374.70857	-27374.69585	-27374.72246	-27374.79683	-27374.76157	-27374.74284	-27374.79525

TableS15: Total electronic energies [E_h] of PaO₂⁺ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

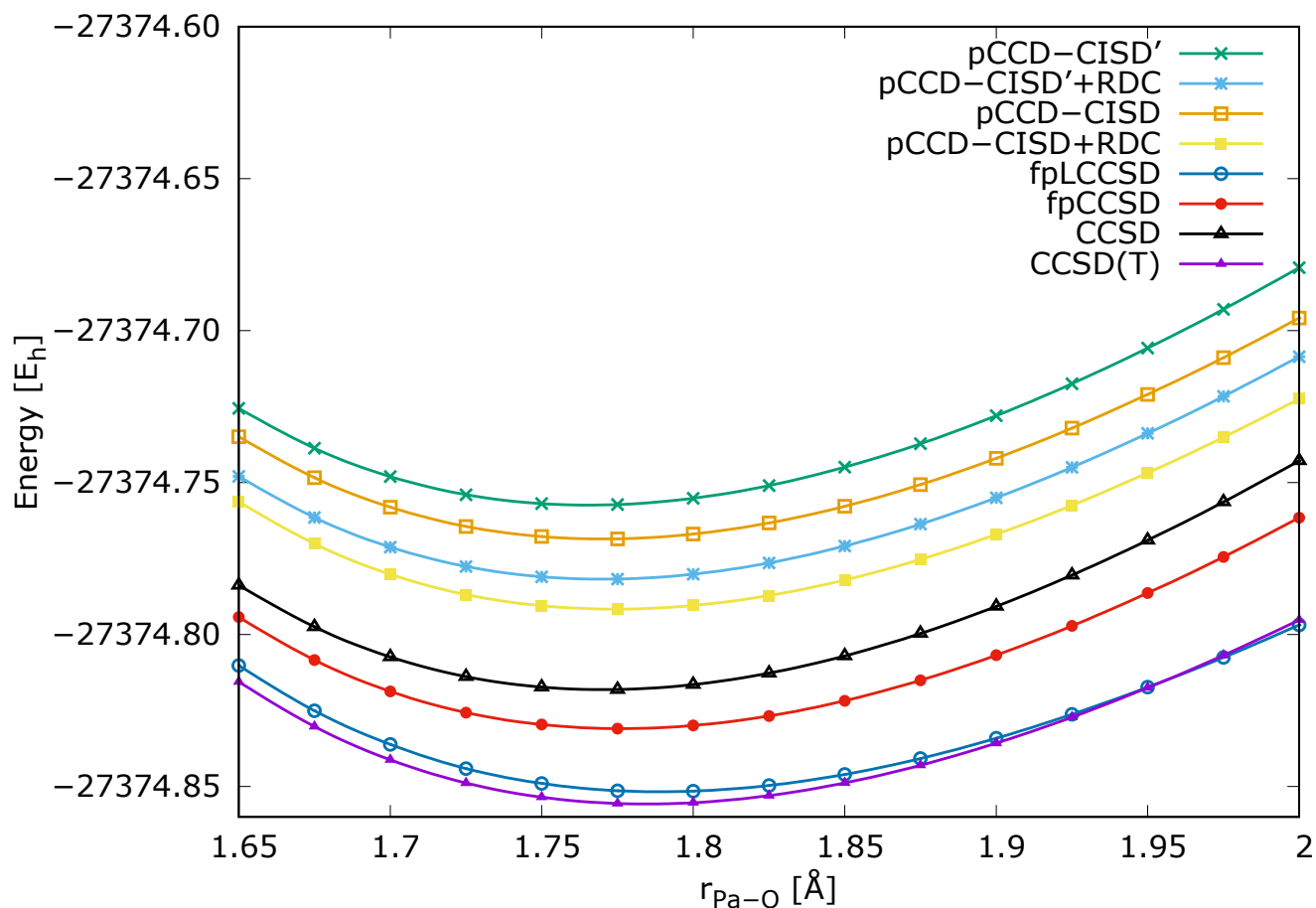


Figure S14: Potential energy surfaces of the ground state of PaO₂⁺ determined for various post-pCCD and conventional CC methods featuring single and double excitations.

S16 Doubles correction for ThO₂

distance	pCCD-CID'	pCCD-CID'+RDC	pCCD-CID	pCCD-CID+RDC	fpLCCD	fpCCD	CCD
1.700	-26614.69026	-26614.70865	-26614.69878	-26614.71644	-26614.75984	-26614.75101	-26614.73991
1.750	-26614.72840	-26614.74701	-26614.73728	-26614.75510	-26614.79892	-26614.78997	-26614.77810
1.800	-26614.75366	-26614.77257	-26614.76287	-26614.78090	-26614.82528	-26614.81617	-26614.80350
1.850	-26614.76803	-26614.78697	-26614.77704	-26614.79522	-26614.83981	-26614.83062	-26614.81828
1.900	-26614.77402	-26614.79355	-26614.78393	-26614.80237	-26614.84786	-26614.83843	-26614.82421
1.950	-26614.77250	-26614.79238	-26614.78289	-26614.80156	-26614.84768	-26614.83806	-26614.82281
2.000	-26614.76488	-26614.78511	-26614.77562	-26614.79452	-26614.84121	-26614.83141	-26614.81535
2.050	-26614.75241	-26614.77302	-26614.76370	-26614.78281	-26614.83014	-26614.82015	-26614.80293
2.100	-26614.73582	-26614.75685	-26614.74766	-26614.76700	-26614.81497	-26614.80479	-26614.78649
2.150	-26614.71610	-26614.73761	-26614.72871	-26614.74827	-26614.79698	-26614.78660	-26614.76680
2.200	-26614.69390	-26614.71594	-26614.70729	-26614.72709	-26614.77654	-26614.76592	-26614.74457
2.250	-26614.66977	-26614.69241	-26614.68405	-26614.70408	-26614.75431	-26614.74343	-26614.72038

TableS16: Total electronic energies [E_h] of ThO₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

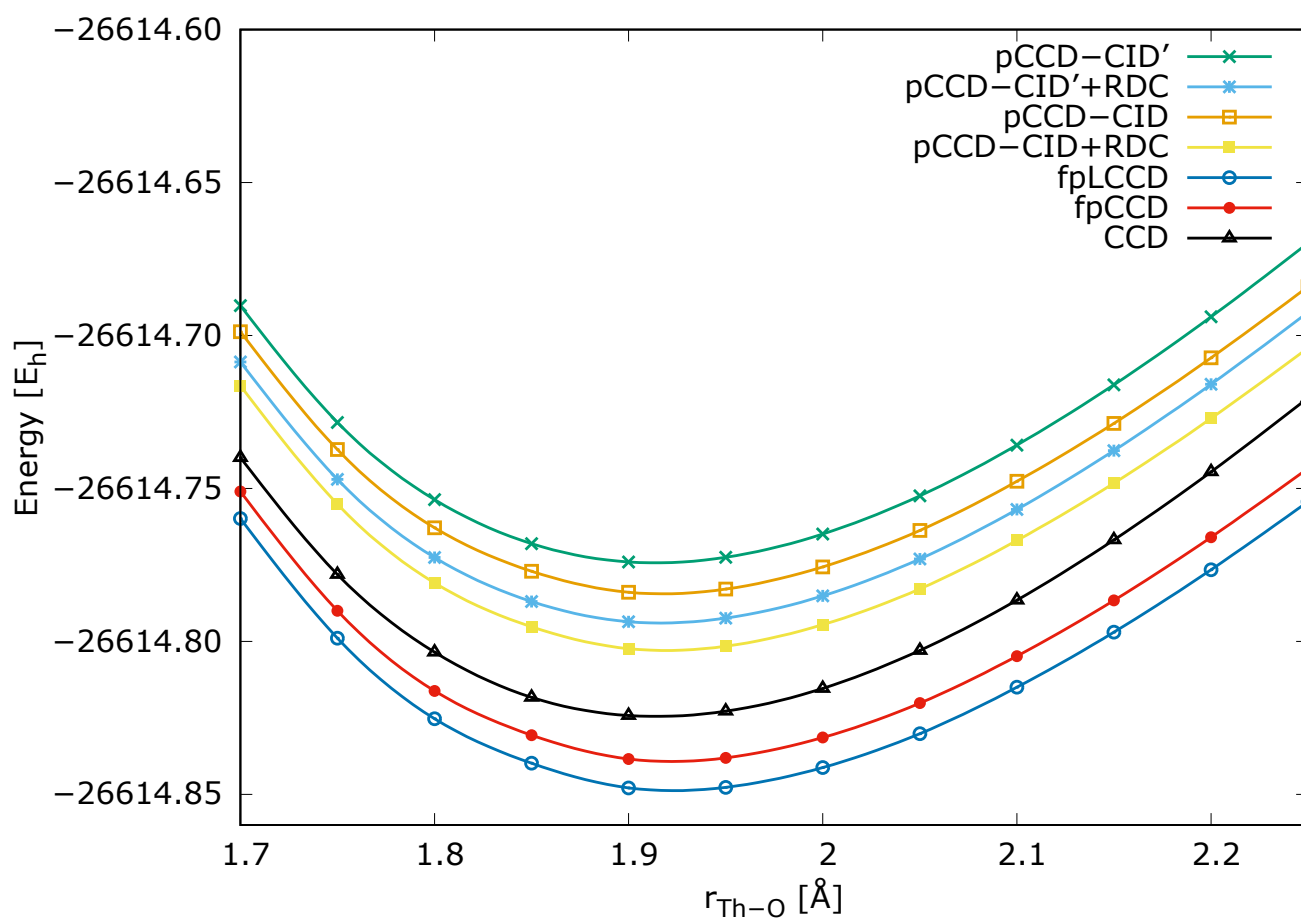


Figure S15: Potential energy surfaces of the ground state of ThO₂ determined for various post-pCCD and conventional CC methods featuring double excitations.

S17 Singles and Doubles correction for ThO₂

distance[Å]	pCCD-CISD'	pCCD-CISD'+RDC	pCCD-CISD	pCCD-CISD+RDC	fpLCCSD	fpCCSD	CCSD	CCSD(T)
1.700	-26614.69463	-26614.71467	-26614.70282	-26614.72225	-26614.77198	-26614.75711	-26614.74828	-26614.77732
1.750	-26614.73292	-26614.75328	-26614.74142	-26614.76113	-26614.81183	-26614.79614	-26614.78697	-26614.81695
1.800	-26614.75830	-26614.77908	-26614.76710	-26614.78714	-26614.83911	-26614.82242	-26614.81288	-26614.84391
1.850	-26614.77297	-26614.79397	-26614.78152	-26614.80189	-26614.85500	-26614.83722	-26614.82817	-26614.86036
1.900	-26614.77894	-26614.80058	-26614.78837	-26614.80910	-26614.86430	-26614.84489	-26614.83463	-26614.86811
1.950	-26614.77752	-26614.79963	-26614.78738	-26614.80849	-26614.86483	-26614.84448	-26614.83378	-26614.86866
2.000	-26614.77004	-26614.79264	-26614.78020	-26614.80169	-26614.86013	-26614.83785	-26614.82689	-26614.86333
2.050	-26614.75770	-26614.78083	-26614.76839	-26614.79026	-26614.85100	-26614.82659	-26614.81505	-26614.85320
2.100	-26614.74128	-26614.76500	-26614.75248	-26614.77476	-26614.83818	-26614.81131	-26614.79921	-26614.83923
2.150	-26614.72170	-26614.74608	-26614.73365	-26614.75636	-26614.82449	-26614.79311	-26614.78017	-26614.82225
2.200	-26614.69962	-26614.72471	-26614.71230	-26614.73545	-26614.81099	-26614.77222	-26614.75861	-26614.80294
2.250	-26614.67560	-26614.70148	-26614.68911	-26614.71269	-26614.79601	-26614.74944	-26614.73509	-26614.78190

TableS17: Total electronic energies [E_h] of ThO₂ obtained for various post-pCCD and CC methods. For all methods, no symmetry constraints were imposed (C1 symmetry).

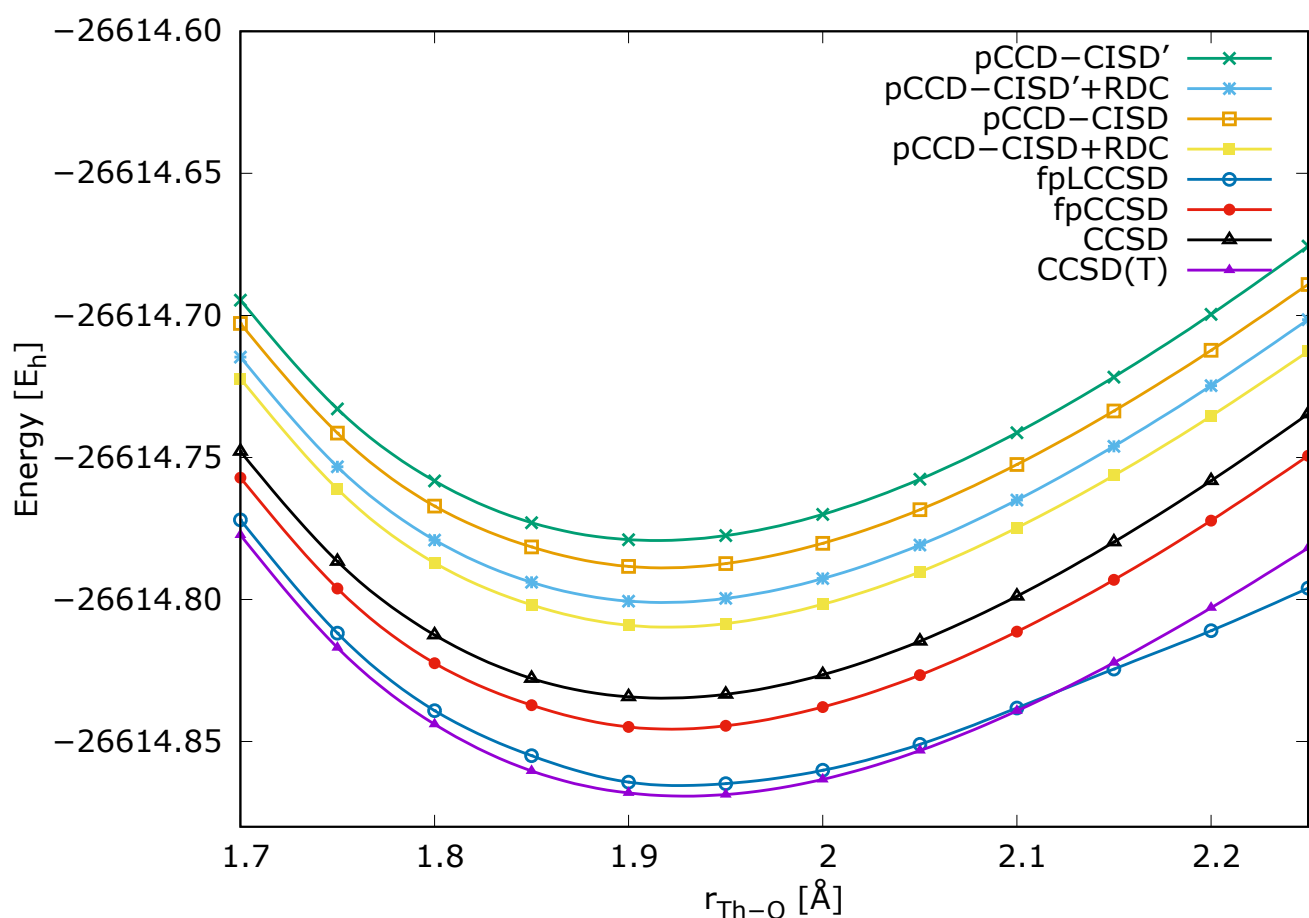


Figure S16: Potential energy surfaces of the ground state of ThO₂ determined for various post-pCCD and conventional CC methods featuring single and double excitations.

S18 Total Energy Mean Error

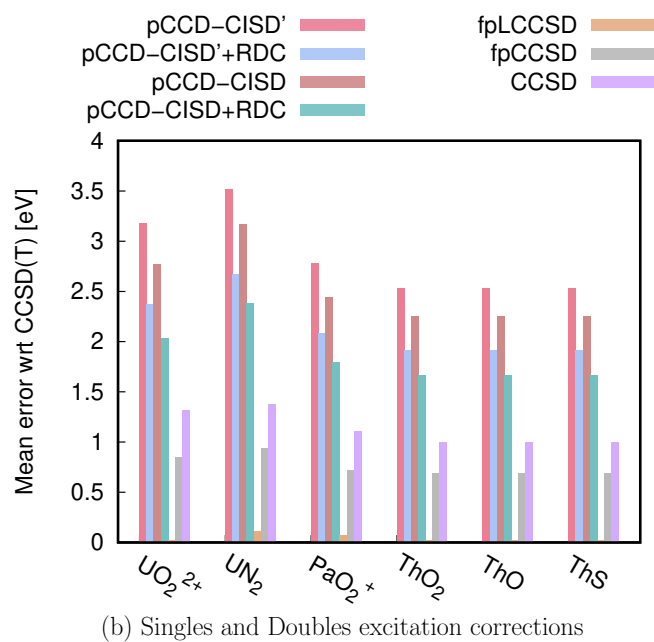
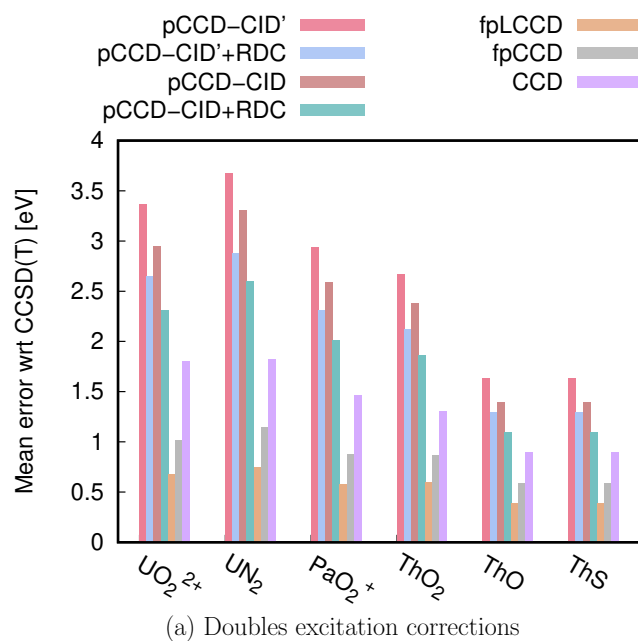


Figure S17: Mean errors in total energies with respect to CR-EOM-CCSD(T) reference data for methods featuring (a) double excitations and (b) single and doubles excitations calculated for all investigate actinide-containing compounds.

S19 Mean errors (ME) and standard deviation (RMSE) in the equilibrium bond distance r_e for the UO_2^{2+} isoelectronic series

Method	ME [Å]	RMSE [Å]
pCCD-CID'	-0.019	±0.020
pCCD-CID'+RDC	-0.015	±0.016
pCCD-CID	-0.015	±0.016
pCCD-CID+RDC	-0.013	±0.014
fpLCCD	-0.006	±0.007
fpCCD	-0.009	±0.009
CCD	-0.018	±0.018
pCCD-CISD'	-0.017	±0.018
pCCD-CISD'+RDC	-0.013	±0.013
pCCD-CISD	-0.014	±0.014
pCCD-CISD+RDC	-0.011	±0.011
fpLCCSD	0.005	±0.006
fpCCSD	-0.008	±0.008
CCSD	-0.013	±0.013

S20 Mean errors (ME) and standard deviation (RMSE) in the harmonic vibrational frequency ω_e for the UO_2^{2+} isoelectronic series

Method	ME [cm^{-1}]	RMSE [cm^{-1}]
pCCD-CID'	52	±58
pCCD-CID'+RDC	42	±47
pCCD-CID	36	±39
pCCD-CID+RDC	30	±32
fpLCCD	13	±13
fpCCD	18	±19
CCD	55	±62
pCCD-CISD'	49	±54
pCCD-CISD'+RDC	35	±39
pCCD-CISD	32	±35
pCCD-CISD+RDC	23	±24
fpLCCSD	-22	±34
fpCCSD	22	±23
CCSD	40	±45

S21 Total energies for electronically excited states in UO_2^{2+}

Table S18: Total electronic energies [E_h] of UO_2^{2+} for different states and various post-pCCD and conventional EOM-CC methods.

distance[Å]	pCCD-CISD*	pCCD-CISD	EOM-fpLCCSD	EOM-CCSD	CR-EOM-CCSD
	$1^1\Phi_g(\sigma_u \rightarrow \phi_u)$				
1.600	-28148.69057	-28148.69057			
1.625	-28148.71046	-28148.71046	-28149.21163		
1.650	-28148.72605	-28148.72605	-28149.22829	-28149.19797	-28149.19402
1.675	-28148.73787	-28148.73787	-28149.24107	-28149.20950	-28149.20492
1.700	-28148.74641	-28148.74641	-28149.25060	-28149.21760	-28149.21238
1.725	-28148.75206	-28148.75206	-28149.25726	-28149.22266	-28149.21680
1.750	-28148.75517	-28148.75517	-28149.26130	-28149.22503	-28149.21855
1.775	-28148.75607	-28148.75607	-28149.26311	-28149.22502	-28149.21792
1.800	-28148.75505	-28148.75505	-28149.26299	-28149.22288	-28149.21519
1.825	-28148.75242	-28148.75242	-28149.26114	-28149.21886	-28149.21062
1.850	-28148.74857	-28148.74857	-28149.25790	-28149.21318	-28149.20442
1.875	-28148.74393	-28148.74393	-28149.25346	-28149.20605	-28149.19682
1.900			-28149.24830	-28149.19764	-28149.18803
	$1^1\Delta_g(\sigma_u \rightarrow \delta_u)$				
1.600	-28148.68177	-28148.68072			
1.625	-28148.70144	-28148.70046	-28149.19965		
1.650	-28148.71689	-28148.71598	-28149.21568	-28149.18534	-28149.18099
1.675	-28148.72868	-28148.72782	-28149.22791	-28149.19639	-28149.19131
1.700	-28148.73728	-28148.73649	-28149.23694	-28149.20409	-28149.19826
1.725	-28148.74314	-28148.74240	-28149.24317	-28149.20883	-28149.20224
1.750	-28148.74663	-28148.74595	-28149.24682	-28149.21095	-28149.20360
1.775	-28148.74811	-28148.74750	-28149.24828	-28149.21077	-28149.20264
1.800	-28148.74794	-28148.74764	-28149.24785	-28149.20855	-28149.19962
1.825	-28148.74724	-28148.74724	-28149.24571	-28149.20457	-28149.19479
1.850	-28148.74488	-28148.74488	-28149.24219	-28149.19904	-28149.18835
1.875	-28148.74049	-28148.74049	-28149.23748	-28149.19219	-28149.18051
1.900			-28149.23204	-28149.18424	-28149.17147
	$2^1\Phi_g(\pi_u \rightarrow \delta_u)$				
1.600					
1.625	-28148.69169	-28148.69169	-28149.15261		
1.650	-28148.70876	-28148.70876	-28149.17019	-28149.14656	-28149.13402
1.675	-28148.72194	-28148.72194	-28149.18376	-28149.16223	-28149.14898
1.700	-28148.73171	-28148.73171	-28149.19664	-28149.17423	-28149.16029
1.725	-28148.73844	-28148.73844	-28149.20633	-28149.18294	-28149.16834
1.750	-28148.74247	-28148.74247	-28149.21302	-28149.18873	-28149.17349
1.775	-28148.74600	-28148.74600	-28149.21706	-28149.19188	-28149.17604
1.800	-28148.74764	-28148.74764	-28149.21870	-28149.19269	-28149.17628
1.825	-28148.74643	-28148.74643	-28149.21806	-28149.19138	-28149.17443
1.850	-28148.74372	-28148.74322	-28149.21538	-28149.18818	-28149.17074
1.875	-28148.73995	-28148.73995	-28149.21073	-28149.18331	-28149.16539
1.900			-28149.20535	-28149.17696	-28149.15860
	$1^1\Pi_g(\pi_u \rightarrow \delta_u)$				
1.600					
1.625	-28148.67875	-28148.67875	-28149.14676		
1.650	-28148.69862	-28148.69862	-28149.16733	-28149.14364	-28149.13121
1.675	-28148.71445	-28148.71445	-28149.18044	-28149.15927	-28149.14615
1.700	-28148.72671	-28148.72671	-28149.19423	-28149.17123	-28149.15742
1.725	-28148.73583	-28148.73583	-28149.20277	-28149.17990	-28149.16544
1.750	-28148.74215	-28148.74215	-28149.20933	-28149.18564	-28149.17055
1.775	-28148.74412	-28148.74412	-28149.21321	-28149.18876	-28149.17306
1.800	-28148.74368	-28148.74368	-28149.21468	-28149.18952	-28149.17326
1.825	-28148.74142	-28148.74142	-28149.21384	-28149.18817	-28149.17138
1.850	-28148.73757	-28148.73757	-28149.21094	-28149.18494	-28149.16765
1.875	-28148.73230	-28148.73230	-28149.20604	-28149.18004	-28149.16229
1.900			-28149.15548		

S22 Excitation energies of UO_2^{2+}

Table S19: Excitation energies [eV] of UO_2^{2+} for different states and various post-pCCD as well as conventional EOM-CC methods.

distance [Å]	pCCD-CISD'	pCCD-CISD	EOM-CCSD		
			EOM-fpLCCSD	EOM-CCSD	CR-EOM-CCSD
$1^1\Phi_g(\sigma_u \rightarrow \phi_u)$					
1.600	16.41	16.67			
1.625	16.19	16.46	4.52		
1.650	15.97	16.25	4.34	4.20	4.31
1.675	15.74	16.03	4.16	3.99	4.11
1.700	15.51	15.82	3.99	3.78	3.92
1.725	15.29	15.61	3.82	3.57	3.73
1.750	15.06	15.41	3.66	3.36	3.54
1.775	14.84	15.20	3.50	3.16	3.35
1.800	14.62	15.00	3.35	2.96	3.17
1.825	14.40	14.80	3.22	2.77	2.99
1.850	14.17	14.59	3.08	2.58	2.82
1.875	13.94	14.38	2.96	2.40	2.65
1.900			2.86	2.23	2.49
$1^1\Delta_g(\sigma_u \rightarrow \delta_u)$					
1.600	16.65	16.94			
1.625	16.44	16.73	4.85		
1.650	16.22	16.52	4.68	4.54	4.66
1.675	15.99	16.31	4.52	4.34	4.48
1.700	15.76	16.09	4.36	4.14	4.30
1.725	15.53	15.88	4.20	3.94	4.12
1.750	15.30	15.66	4.05	3.75	3.95
1.775	15.06	15.43	3.90	3.55	3.77
1.800	14.81	15.20	3.77	3.35	3.59
1.825	14.54	14.94	3.64	3.16	3.42
1.850	14.27	14.69	3.51	2.97	3.26
1.875	14.03	14.47	3.40	2.78	3.09
1.900			3.30	2.59	2.94
$2^1\Phi_g(\pi_u \rightarrow \delta_u)$					
1.600					
1.625	16.70	16.97	6.13		
1.650	16.44	16.72	5.92	5.60	5.94
1.675	16.17	16.47	5.72	5.27	5.63
1.700	15.91	16.22	5.45	4.96	5.34
1.725	15.66	15.98	5.20	4.65	5.05
1.750	15.41	15.75	4.97	4.35	4.76
1.775	15.11	15.48	4.75	4.06	4.49
1.800	14.82	15.20	4.56	3.78	4.23
1.825	14.56	14.96	4.39	3.52	3.98
1.850	14.31	14.74	4.24	3.26	3.74
1.875	14.05	14.48	4.12	3.02	3.51
1.900			4.03	2.79	3.29
$1^1\Pi_g(\pi_u \rightarrow \delta_u)$					
1.600					
1.625	17.05	17.32	6.29		
1.650	16.71	16.99	6.00	5.68	6.02
1.675	16.38	16.67	5.81	5.35	5.71
1.700	16.05	16.36	5.52	5.04	5.41
1.725	15.73	16.06	5.30	4.73	5.13
1.750	15.42	15.76	5.07	4.43	4.84
1.775	15.17	15.53	4.86	4.15	4.57
1.800	14.93	15.31	4.67	3.87	4.31
1.825	14.70	15.10	4.50	3.60	4.06
1.850	14.47	14.89	4.36	3.35	3.82
1.875	14.26	14.69	4.25	3.11	3.59
1.900			4.16	2.88	3.37

References

- [1] K. A. Peterson, A. K. Wilson, D. E. Woon and T. H. Dunning Jr., *Theor. Chem. Acc.*, 1997, **97**, 251–259.