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Density Matrix Renormalization Group Pair-Density Functional Theory (DMRG-PDFT): Singlet–Triplet Gaps in Polyacenes and Polyacetylenes

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Table S1. Absolute energies for DMRG and DMRG-PDFT in Hartrees for vertical S-T gaps for polyacenes.

***n*-acene**	**Spin state**	**Active - space**	***M***	**DMRG**	**DMRG-PDFT**
2-acene	Triplet	(10, 10)	100	-383.387011	-385.192050
2-acene	Triplet	(10, 10)	200	-383.388475	-385.189633
2-acene	Triplet	(10, 10)	300	-383.388489	-385.189603
2-acene	Triplet	(10, 10)	500	-383.388489	-385.189603
2-acene	Triplet	(10, 10)	1000	-383.388489	-385.189603
2-acene	Singlet	(10, 10)	100	-383.500160	-385.313681
2-acene	Singlet	(10, 10)	200	-383.500679	-385.312667
2-acene	Singlet	(10, 10)	300	-383.500691	-385.312633
2-acene	Singlet	(10, 10)	500	-383.500691	-385.312633
2-acene	Singlet	(10, 10)	1000	-383.500691	-385.312633
2-acene	Singlet	(10, 20)	100	-383.517450	-385.317672
2-acene	Triplet	(10, 20)	100	-383.399425	-385.200343
2-acene	Singlet	(10, 20)	500	-383.525466	-385.312135
2-acene	Triplet	(10, 20)	500	-383.410957	-385.191529
2-acene	Singlet	(10, 20*)	500	-383.517990	-385.313060
2-acene	Triplet	(10, 20*)	500	-383.403857	-385.190442
3-acene	Triplet	(14, 14)	100	-536.100900	-538.654200
3-acene	Triplet	(14, 14)	200	-536.109200	-538.647900
3-acene	Triplet	(14, 14)	300	-536.112800	-538.644200
3-acene	Triplet	(14, 14)	500	-536.115900	-538.640400
3-acene	Triplet	(14, 14)	1000	-536.117600	-538.637300
3-acene	Triplet	(14, 14)	2000	-536.118000	-538.636200
3-acene	Singlet	(14, 14)	100	-536.191200	-538.737900
3-acene	Singlet	(14, 14)	200	-536.198100	-538.730900
3-acene	Singlet	(14, 14)	300	-536.200300	-538.728200

3-acene	Singlet	(14, 14)	500	-536.201700	-538.725900
3-acene	Singlet	(14, 14)	1000	-536.202500	-538.724200
3-acene	Singlet	(14, 14)	2000	-536.202700	-538.723800
4-acene	Triplet	(18,18)	500	-688.825271	-692.086857
4-acene	Singlet	(18,18)	500	-688.894332	-692.144985
5-acene	Triplet	(22, 22)	500	-841.532300	-845.532000
5-acene	Singlet	(22, 22)	500	-841.577800	-845.567900
6-acene	Triplet	(26, 26)	500	-994.209879	-998.964357
6-acene	Singlet	(26, 26)	500	-994.253558	-998.993342
7-acene	Triplet	(30, 30)	500	-1146.893043	-1152.399190
7-acene	Singlet	(30, 30)	500	-1146.922746	-1152.421666

Note: (10, 20) ≡(10, 20 :ππ*2π*) and (10, 20*) ≡ (10, 20: ππ*σ*)

Table S2. Absolute energies for DMRG and DMRG-PDFT in Hartrees for adiabatic S-T gaps for polyacenes

***n*-acene**	**Spin state**	**Active-space**	***M***	**DMRG**	**DMRG-PDFT**
2-acene	Triplet	(10, 10)	100	-383.402018	-385.207464
2-acene	Triplet	(10, 10)	200	-383.403057	-385.205917
2-acene	Triplet	(10, 10)	300	-383.403065	-385.205895
2-acene	Triplet	(10, 10)	500	-383.403065	-385.205895
2-acene	Triplet	(10, 10)	1000	-383.403065	-385.205895
2-acene	Triplet	(10, 20)	100	-383.425105	-385.207451
2-acene	Triplet	(10, 20)	500	-383.425105	-385.207451
2-acene	Triplet	(10, 20*)	500	-383.418488	-385.206737
3-acene	Triplet	(14, 14)	100	-536.115900	-538.664200
3-acene	Triplet	(14, 14)	200	-536.123200	-538.658600
3-acene	Triplet	(14, 14)	300	-536.126600	-538.655400
3-acene	Triplet	(14, 14)	500	-536.129200	-538.652300
3-acene	Triplet	(14, 14)	1000	-536.130600	-538.649800

3-acene	Triplet	(14, 14)	2000	-536.131000	-538.648900
4-acene	Triplet	(18,18)	500	-688.837735	-692.094622
5-acene	Triplet	(22, 22)	500	-841.532300	-845.532000
6-acene	Triplet	(26, 26)	500	-994.219323	-998.966566
7-acene	Triplet	(30, 30)	500	-1146.898064	-1152.398852

Note: (10, 20) ≡(10, 20 :ππ*2π*) and (10, 20*) ≡ (10, 20: ππ*σ*)

Table S3. Absolute energies for DMRG and DMRG-PDFT in Hartrees for vertical S-T gaps for *n*-polyacetylenes

n	***M***	**DMRG**		**tPBE**	
		S	**T**	**S**	**T**
2	**10**	-231.909738	-231.806787	-233.034404	-232.931874
	20	-231.909738	-231.806787	-233.034404	-232.931874
	50	-231.909738	-231.806787	-233.034404	-232.931874
	100	-231.909738	-231.806787	-233.034404	-232.931874
	500	-231.909738	-231.806787	-233.034404	-232.931874
	1000	-231.909738	-231.806787	-233.034404	-232.931874
3	**10**	-231.909738	-231.806787	-233.036100	-232.933787
	20	-231.911517	-231.808628	-233.034404	-232.931874
	50	-231.911517	-231.808628	-233.034404	-232.931874
	100	-231.911517	-231.808628	-233.034404	-232.931874
	500	-231.911517	-231.808575	-233.034404	-232.931874
	1000	-231.911517	-231.808575	-233.034404	-232.931874
4	**10**	-308.818458	-308.716125	-310.331340	-310.244237
	20	-308.827789	-308.735682	-310.327045	-310.241257
	50	-308.832396	-308.742920	-310.322311	-310.235252
	100	-308.832488	-308.743005	-310.322142	-310.235121
	500	-308.832488	-308.743005	-310.322142	-310.235121
	1000	-308.832488	-308.743005	-310.322142	-310.235121
5	**10**	-385.717914	-385.622614	-387.621768	-387.547175
	20	-385.740515	-385.648237	-387.620513	-387.548729
	50	-385.749642	-385.665635	-387.614405	-387.541102
	100	-385.753077	-385.671447	-387.610764	-387.535877
	500	-385.753473	-385.673106	-387.610083	-387.533515
	1000	-385.753473	-385.673106	-387.610083	-387.533515
6	**10**	-462.620760	-462.506609	-464.913481	-464.855461
	20	-462.650284	-462.551896	-464.916490	-464.850096
	50	-462.662533	-462.581531	-464.909040	-464.843820

	100	-462.670096	-462.591472	-464.903034	-464.838521
	500	-462.674399	-462.600396	-464.898159	-464.829400
	1000	-462.674421	-462.600578	-464.898103	-464.829012
7	**10**	-539.499629	-539.409086	-542.210914	-542.154255
	50	-539.572313	-539.492427	-542.206087	-542.147232
	100	-539.582893	-539.506289	-542.198222	-542.140194
	500	-539.594474	-539.523964	-542.187728	-542.126527
	1000	-539.595218	-539.525799	-542.186430	-542.123749
8	**10**	-616.389661	-616.289863	-619.508470	-619.459139
	50	-616.482067	-616.402558	-619.502222	-619.446348
	100	-616.494260	-616.417665	-619.493725	-619.441004
	500	-616.513071	-616.443785	-619.479207	-619.424189
	1000	-616.515178	-616.448084	-619.476141	-619.419716
9	**10**	-693.261647	-693.184342	-696.801510	-696.740559
	50	-693.380535	-693.296666	-696.793559	-696.740411
	100	-693.403882	-693.325120	-696.786224	-696.735581
	500	-693.429762	-693.360582	-696.771130	-696.720473
	1000	-693.433813	-693.367528	-696.766798	-696.715504
15	**10**	-1154.215940	-1154.142016	-1160.324138	-1160.278388
	50	-1154.665011	-1154.571177	-1160.589496	-1160.543866
	100	-1154.793900	-1154.687067	-1160.594827	-1160.548139
	500	-1154.832457	-1154.752990	-1160.586230	-1160.546262
	1000	-1154.889654	-1154.812515	-1160.555271	-1160.517261

Table S4. Absolute energies for CASSCF, CASPT2, and MC-PDFT in Hartrees for vertical S-T gaps for *n*-polyacetylenes[a]

n	**Spin state**	**Active space**	**CASSCF**	**CASPT2**	**MC-PDFT**
1	Singlet	(2,2)	-78.070184	-78.321268	-78.070184
1	Triplet	(2, 2)	-77.910609	-78.154313	-78.289453
2	Singlet	(4, 4)	-154.99066	-155.47975	-155.74711
2	Triplet	(4, 4)	-154.86664	-155.35556	-155.61985
3	Singlet	(6, 6)	-231.91152	-232.638264	-233.034404
3	Triplet	(6, 6)	-231.80863	-232.537893	-232.931874
4	Singlet	(8, 8)	-308.832488	-309.797215	-310.322141
4	Triplet	(8, 8)	-308.693791	-309.660058	-310.182450
5	Singlet	(10, 10)	-385.753473	-386.956445	-387.610082
5	Triplet	(10, 10)	-385.673106	-386.880315	-387.533515
6	Singlet	(12, 12)	-462.674421	-464.115744	-464.898098
6	Triplet	(12, 12)	-462.600578	-464.046516	-464.829010
7	Singlet	(14, 14)	-539.595331	-541.275123	-542.186155
7	Triplet	(14, 14)	-539.526334	-541.210963	-542.122632
8	Singlet	(16, 16)	-616.516208	-618.4345088	-619.474222
8	Triplet	(16, 16)	-616.450914	-618.3742628	-619.414971

[a]Hartree-Fock orbitals were used as the guess orbitals for all the calculations. Sweeps 4, 5, and 6 were used for all the calculations except for 6-acene and 7-acene, and we found no change with respect to changing the number of sweeps. We used 6 sweeps for 6-acene and 7-acene.

Table S5 Vertical and adiabatic singlet–triplet gap ($E_{triplet} - E_{singlet}$, in eV) for naphthalene for (10, 10: ππ*) (or simply (10, 10), (10, 20 :ππ*2π*), and (10, 20: ππ*σ*) active spaces.

Active Space	*M*	DMRG		DMRG-PDFT		Reference values	
		Vert.	Ad.	Vert.	Ad.	Vert.	Ad.
						3.43, 3.30	2.78, 2.79
(10,10)	100	3.08	2.67	3.31	2.89		
(10, 20 :ππ*2π*)	100	3.21	2.51	3.19	3.00		
(10, 10)	500	3.05	2.66	3.35	2.91		
(10, 20: ππ*2π*)	500	3.12	2.73	3.28	2.85		
(10, 20: ππ*σ*)	500	3.11	2.71	3.34	2.89		

For small (*M* = 100), DMRG-PDFT shows lower active-space dependence than does DMRG alone. At *M* = 500, for three different active-spaces, that is, (10, 10), (10, 20 :ππ*2π*), and (10, 20: ππ*σ*) DMRG-PDFT singlet–triplet gap varies within the samll range of 0.07eV. It is encouraging that the expansion of the active-space results in singlet-triplet gaps closer to the experimental values (2.78-2.79 eV) for *M* = 500.

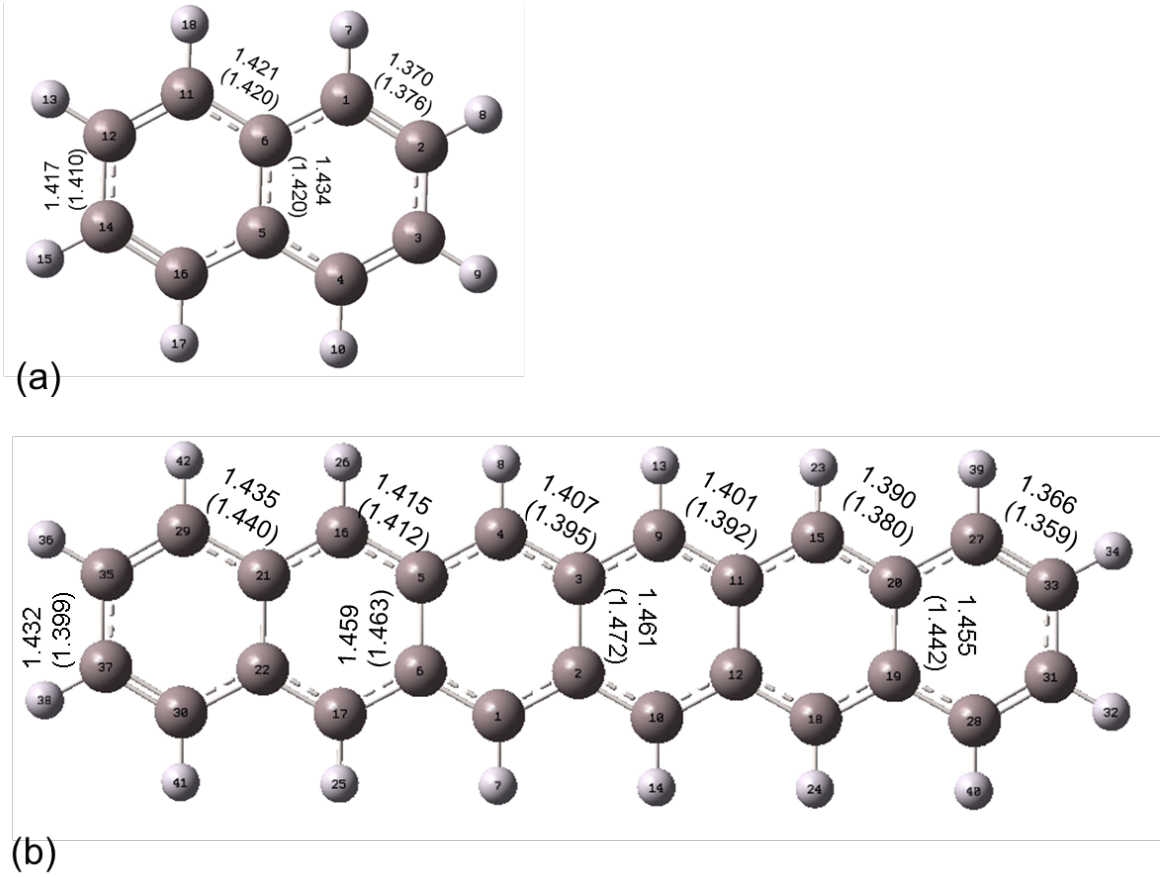

Figure S1. Comparison between calculated and experimental geometries (B3LYP/6-31G(d,p)) of naphthalene and hexacene. The mean deviation in bond lengths are 0.007 and 0.011 Å, respectively.

Table S6. Atomic coordinates for *n*-polyacetylenes $(H_2C{=}CH_2)_n$, optimized by B3LYP/6-31G(d,p). XYZ Cartesian coordinates are in Angstroms.

***n* = 1**

C	-0.662958	0.000000	0.000000
C	0.662958	0.000000	0.000000
H	-1.256559	-0.924026	0.000000
H	1.256559	-0.924026	0.000000
H	-1.256559	0.924026	0.000000
H	1.256559	0.924026	0.000000

***n* = 2**

C	1.855098	0.114866	0.000000
C	-1.855098	-0.114866	0.000000
C	0.643269	-0.423208	0.000000
C	-0.643269	0.423208	0.000000
H	2.022642	1.200276	0.000000
H	-2.022642	-1.200276	0.000000
H	2.772605	-0.488763	0.000000
H	-2.772605	0.488763	0.000000
H	0.475726	-1.508617	0.000000
H	-0.475726	1.508617	0.000000

***n* = 3**

C	-3.075055	0.167498	0.000000
C	3.075055	-0.167498	0.000000
C	-1.867388	-0.418911	0.000000
C	1.867388	0.418911	0.000000
H	-3.180907	1.249260	0.000000
H	3.180907	-1.249260	0.000000
H	-3.991128	-0.413469	0.000000
H	3.991128	0.413469	0.000000
H	-1.805249	-1.507080	0.000000

H	1.805249	1.507080	0.000000
C	-0.606997	0.297372	0.000000
C	0.606997	-0.297372	0.000000
H	-0.661631	1.386399	0.000000
H	0.661631	-1.386399	0.000000

***n* = 4**

C	-4.308669	0.197146	0.000000
C	4.308669	-0.197146	0.000000
C	-3.110874	-0.411353	0.000000
C	3.110874	0.411353	0.000000
H	-4.394907	1.280613	0.000000
H	4.394907	-1.280613	0.000000
H	-5.234940	-0.367304	0.000000
H	5.234940	0.367304	0.000000
H	-3.069439	-1.500574	0.000000
H	3.069439	1.500574	0.000000
C	-1.839087	0.279751	0.000000
C	1.839087	-0.279751	0.000000
C	-0.634371	-0.341144	0.000000
C	0.634371	0.341144	0.000000
H	-1.871161	1.369551	0.000000
H	1.871161	-1.369551	0.000000
H	-0.607249	-1.431263	0.000000
H	0.607249	1.431263	0.000000

***n* = 5**

C	-5.544122	0.214299	0.000000
C	5.544122	-0.214299	0.000000
C	-4.350171	-0.402736	0.000000
C	4.350171	0.402736	0.000000
H	-5.622764	1.298325	0.000000

H	5.622764	-1.298325	0.000000
H	-6.474236	-0.343751	0.000000
H	6.474236	0.343751	0.000000
H	-4.316850	-1.492261	0.000000
H	4.316850	1.492261	0.000000
C	-3.074155	0.278469	0.000000
C	3.074155	-0.278469	0.000000
C	-1.872943	-0.352359	0.000000
C	1.872943	0.352359	0.000000
H	-3.097453	1.368452	0.000000
H	3.097453	-1.368452	0.000000
H	-1.855664	-1.442745	0.000000
H	1.855664	1.442745	0.000000
C	-0.600949	0.317418	0.000000
C	0.600949	-0.317418	0.000000
H	-0.616498	1.407635	0.000000
H	0.616498	-1.407635	0.000000

***n* = 6**

C	-6.780165	0.224843	0.000000
C	6.780165	-0.224843	0.000000
C	-5.587871	-0.395931	0.000000
C	5.587871	0.395931	0.000000
H	-6.855486	1.309093	0.000000
H	6.855486	-1.309093	0.000000
H	-7.711938	-0.330412	0.000000
H	7.711938	0.330412	0.000000
H	-5.558134	-1.485572	0.000000
H	5.558134	1.485572	0.000000
C	-4.310074	0.280869	0.000000
C	4.310074	-0.280869	0.000000

C	-3.110354	-0.354381	0.000000
C	3.110354	0.354381	0.000000
H	-4.329470	1.370910	0.000000
H	4.329470	-1.370910	0.000000
H	-3.097480	-1.444853	0.000000
H	3.097480	1.444853	0.000000
C	-1.837018	0.309854	0.000000
C	1.837018	-0.309854	0.000000
C	-0.636207	-0.330789	0.000000
C	0.636207	0.330789	0.000000
H	-1.847524	1.400093	0.000000
H	1.847524	-1.400093	0.000000
H	-0.626779	-1.421145	0.000000
H	0.626779	1.421145	0.000000

***n* = 7**

C	-8.016413	0.231484	0.000000
C	8.016413	-0.231484	0.000000
C	-6.824842	-0.390985	0.000000
C	6.824842	0.390985	0.000000
H	-8.090236	1.315832	0.000000
H	8.090236	-1.315832	0.000000
H	-8.948930	-0.322511	0.000000
H	8.948930	0.322511	0.000000
H	-6.796748	-1.480677	0.000000
H	6.796748	1.480677	0.000000
C	-5.546279	0.283772	0.000000
C	5.546279	-0.283772	0.000000
C	-4.347190	-0.353545	0.000000
C	4.347190	0.353545	0.000000
H	-5.563863	1.373834	0.000000

H	5.563863	-1.373834	0.000000
H	-4.336393	-1.444053	0.000000
H	4.336393	1.444053	0.000000
C	-3.073314	0.308052	0.000000
C	3.073314	-0.308052	0.000000
C	-1.872942	-0.335356	0.000000
C	1.872942	0.335356	0.000000
H	-3.081425	1.398294	0.000000
H	3.081425	-1.398294	0.000000
H	-1.866428	-1.425761	0.000000
H	1.866428	1.425761	0.000000
C	-0.600391	0.322405	0.000000
C	0.600391	-0.322405	0.000000
H	-0.606257	1.412748	0.000000
H	0.606257	-1.412748	0.000000

***n* = 8**

H	4.316637	-1.398630	0.000000
H	-4.316637	1.398630	0.000000
H	3.104331	1.426781	0.000000
H	-3.104331	-1.426781	0.000000
H	1.841023	-1.409856	0.000000
H	-1.841023	1.409856	0.000000
H	0.632466	1.417725	0.000000
H	-0.632466	-1.417725	0.000000
H	9.325912	-1.320043	0.000000
H	-9.325912	1.320043	0.000000
H	10.185553	0.317808	0.000000
H	-10.185553	-0.317808	0.000000
H	8.034061	1.477254	0.000000
H	-8.034061	-1.477254	0.000000

H	6.799346	-1.376374	0.000000
H	-6.799346	1.376374	0.000000
H	5.573884	1.442478	0.000000
H	-5.573884	-1.442478	0.000000
C	9.252725	-0.235656	0.000000
C	-9.252725	0.235656	0.000000
C	4.309669	-0.308390	0.000000
C	-4.309669	0.308390	0.000000
C	3.109422	0.336355	0.000000
C	-3.109422	-0.336355	0.000000
C	1.836908	-0.319522	0.000000
C	-1.836908	0.319522	0.000000
C	0.636059	0.327343	0.000000
C	-0.636059	-0.327343	0.000000
C	8.061436	0.387540	0.000000
C	-8.061436	-0.387540	0.000000
C	6.782578	-0.286305	0.000000
C	-6.782578	0.286305	0.000000
C	5.583715	0.351954	0.000000
C	-5.583715	-0.351954	0.000000