General formulation of spin-flip time-dependent density functional theory using non-collinear kernels: Theory, implementation, and benchmarks. Supplementary Materials.

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This document contains $< S^2 >$ values for the diradical states computed by SF methods as well as Cartesian geometries and nuclear repulsion energies for all molecular systems. In addition, the details of the SF-CCSD and SF-CCSD(dT) calculations are summarized for each system.

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I. $< S^2 >$ VALUES FOR TARGET SPIN-FLIP STATES IN DIRADICALS

TABLE I. $\langle S^2 \rangle$ values for selected atoms.

	C		N		O		Si		P		S	
	^3P	^1D	^4S	^2D	^3P	^1D	^3P	^1D	^4S	^2D	^3P	^1D
C-5050	2.0086	0.0118	3.7542	0.7603	2.0074	0.0084	2.0134	0.0161	3.7489	0.7597	2.0114	0.0131
C-PBE50	2.0094	0.0106	3.7542	0.7587	2.0075	0.0081	2.0173	0.0170	3.7499	0.7584	2.0137	0.0139
LDA	2.0065	0.0066	3.7567	0.7576	2.0078	0.0052	2.0044	0.0066	3.7511	0.7554	2.0059	0.0061
BLYP	2.0067	0.0067	3.7566	0.7561	2.0074	0.0050	2.0062	0.0063	3.7512	0.7539	2.0071	0.0063
B3LYP	2.0086	0.0079	3.7576	0.7571	2.0086	0.0058	2.0093	0.0096	3.7511	0.7558	2.0092	0.0087
NC-5050	2.0118	0.0105	3.7593	0.7589	2.0110	0.0075	2.0145	0.0155	3.7511	0.7593	2.0131	0.0134
BHHLYP	2.0116	0.0104	3.7592	0.7586	2.0109	0.0074	2.0145	0.0151	3.7510	0.7588	2.0129	0.0131
B97	2.0130	0.0079	3.7620	0.7590	2.0127	0.0066	2.0118	0.0089	3.7545	0.7578	2.0124	0.0097
ωB97	2.0125	0.0121	3.7639	0.7638	2.0153	0.0083	2.0050	0.0171	3.7493	0.7645	2.0134	0.0128
ωB97X	2.0158	0.0108	3.7650	0.7625	2.0142	0.0073	2.0094	0.0139	3.7540	0.7604	2.0134	0.0108
BP86	2.0071	0.0068	3.7557	0.7562	2.0072	0.0053	2.0083	0.0098	3.7504	0.7558	2.0089	0.0085
B3P86	2.0090	0.0085	3.7570	0.7575	2.0087	0.0063	2.0114	0.0132	3.7507	0.7581	2.0110	0.0112
PW91	2.0075	0.0064	3.7553	0.7557	2.0077	0.0052	2.0084	0.0095	3.7493	0.7554	2.0092	0.0087
B3PW91	2.0090	0.0087	3.7565	0.7573	2.0088	0.0064	2.0126	0.0147	3.7503	0.7585	2.0117	0.0119
PBE	2.0072	0.0064	3.7553	0.7556	2.0076	0.0052	2.0089	0.0099	3.7498	0.7557	2.0094	0.0089
PBE0	2.0097	0.0088	3.7565	0.7571	2.0094	0.0066	2.0140	0.0154	3.7501	0.7588	2.0129	0.0130
PBE50	2.0125	0.0117	3.7578	0.7589	2.0113	0.0083	2.0196	0.0219	3.7503	0.7625	2.0169	0.0178
ωPBEh	2.0090	0.0089	3.7557	0.7569	2.0090	0.0064	2.0157	0.0177	3.7498	0.7596	2.0129	0.0133

TABLE II. $\langle S^2 \rangle$ values for the three lowest states of CH_2, NH_2^+, SiH_2, PH_2^+.

	CH_2				NH_2^+				SiH_2				PH_2^+			
	$^3B_1$	$^1A_1$	$^1B_1$	$^1A_1$	$^3B_1$	$^1A_1$	$^1B_1$	$^1A_1$	$^1A_1$	$^3B_1$	$^1B_1$	$^1A_1$	$^1A_1$	$^3B_1$	$^1B_1$	$^1A_1$ 1
C-5050	2.0132	0.0134	0.0182	0.0221	2.0204	0.0111	0.017 0	0.018	0.0101	2.0053	0.0275	0.0830	0.0091	2.0078	0.0224	0.0256
C-PBE50	2.0142	0.0152	0.0216	0.0244	2.0232	0.0125	0.0184	0.0193	0.0118	2.0079	0.0296	0.0782	0.0113	2.0072	0.0290	0.0300
LDA	2.0129	0.0131	0.0102	0.0157	2.0159	0.0100	0.0092	0.0126	0.0092	2.0050	0.0125	0.0105	0.0079	2.0059	0.0106	0.0111
BLYP	2.0081	0.0132	0.0136	0.0204	2.0073	0.0098	0.0104	0.0158	0.0077	2.0031	0.0125	0.0165	0.0068	2.0017	0.0128	0.0141
B3LYP	2.0120	0.0128	0.0141	0.0204	2.0191	0.0098	0.0121	0.0161	0.0085	2.0043	0.0176	0.0385	0.0076	2.0054	0.0155	0.0169
NC-5050	2.0151	0.0125	0.0170	0.0221	2.0271	0.0105	0.0158	0.0180	0.0097	2.0054	0.0270	0.0799	0.0091	2.0089	0.0219	0.0252
BHHLYP	2.0145	0.0123	0.1976	0.0221	2.0253	0.0103	0.0158	0.0182	0.0097	2.0039	0.0280	0.0777	0.0089	2.0086	0.0215	0.0256
B97	2.0035	0.0123	0.0226	0.0286	2.0225	0.0108	0.0127	0.0197	0.0066	1.9791	0.0371	0.0206	0.0072	2.0062	0.0142	0.0196
ωB97	1.9209	0.0115	0.0652	0.0286	2.0199	0.0114	0.0142	0.0228	0.0067	1.8461	0.1546	0.0206	0.0055	1.4376	0.3738	0.0192
ωB97X	1.9512	0.0179	0.0564	0.0386	2.0210	0.0131	0.0142	0.0240	0.0116	1.8343	0.1729	0.0233	0.0072	1.8967	0.1223	0.0208
BP86	2.0150	0.0163	0.0139	0.0218	2.0187	0.0113	0.0114	0.0160	0.0129	2.0049	0.0213	0.0256	0.0112	2.0056	0.0191	0.0199
B3P86	2.0170	0.0155	0.0154	0.0220	2.0222	0.0114	0.0134	0.0166	0.0124	2.0063	0.0282	0.0487	0.0112	2.0076	0.0214	0.0200
PW91	2.0158	0.0158	0.0140	0.0245	2.0192	0.0114	0.0118	0.0174	0.0127	2.0037	0.0207	0.0201	0.0114	2.0050	0.0197	0.0217
B3PW91	2.0180	0.0162	0.0161	0.0217	2.0233	0.0119	0.0140	0.0169	0.0146	2.0073	0.0274	0.0647	0.0128	2.0087	0.0237	0.0217
PBE	2.0149	0.0150	0.0137	0.0220	2.0197	0.0111	0.0177	0.0163	0.0122	2.0044	0.0208	0.0180	0.0113	2.0057	0.0193	0.0220
PBE0	2.0189	0.0151	0.0164	0.0228	2.0246	0.0117	0.0147	0.0175	0.0130	2.0071	0.0267	0.0494	0.0123	2.0088	0.0242	0.0440
PBE50	2.0226	0.0156	0.0198	0.0244	2.0309	0.0128	0.0184	0.0193	0.0140	2.0093	0.0350	0.1196	0.0137	2.0121	0.0311	0.0299
ωPBEh	2.0182	0.0153	0.0163	0.0233	2.0242	0.0117	0.0143	0.0174	0.0134	2.0084	0.0290	0.0664	0.0126	2.0098	0.0246	0.0238

TABLE III. $\langle S^2 \rangle$ values for three diradicals (unpaired electrons on the same center) from the ring opening of cyclohexane and methylcyclohexane.

	C6rr				C7rr				C6rrC			
	$^1A_1$	$^3B_1$	$^1B_1$	$^1A_1$	$^1A_1$	$^3B_1$	$^1B_1$	$^1A_1$	$^1A_1$	$^3B_1$	$^1B_1$	$^1A_1$
C-5050	0.0191	2.0131	0.0272	0.3090	0.0191	2.0131	0.0272	0.4597	0.0214	2.0152	0.0292	0.0505
C-PBE50	0.0230	2.0044	0.0431	0.3541	0.0230	2.0042	0.0433	0.2517	0.0256	2.0091	0.0430	0.0643
LDA	0.0170	2.0123	0.0168	0.3398	0.0170	2.0123	0.0168	0.2718	0.0175	2.0122	0.0157	0.5565
BLYP	0.0203	1.9997	0.0300	0.1887	0.0203	1.9997	0.0301	0.4559	0.0217	2.0017	0.0286	0.2434
B3LYP	0.0184	2.0073	0.0267	0.0739	0.0186	2.0074	0.0264	0.0717	0.0201	2.0098	0.0262	0.2066
NC-5050	0.0179	2.0136	0.0289	0.5720	0.0179	2.0135	0.0290	0.3587	0.0202	2.0171	0.0294	0.0546
BHHLYP	0.0179	2.0095	0.0324	0.4610	0.0182	2.0100	0.0348	0.2263	0.0203	2.0139	0.0324	0.0547
B97	0.0204	1.9701	0.0710	0.0925	0.0208	1.9705	0.0715	0.1024	0.0229	1.9630	0.0819	0.1356
ωB97	0.0199	1.7032	0.3368	0.0476	0.0199	1.7006	0.3397	0.0482	0.0420	2.0072	0.3129	0.1133
ωB97X	0.0267	1.8227	0.2270	0.0709	0.0275	1.8423	0.2644	0.1480	0.0293	1.8221	0.2286	0.4956
BP86	0.0239	2.0116	0.0224	0.5839	0.0241	2.0118	0.0228	0.4783	0.0236	2.0139	0.0224	0.4926
B3P86	0.0213	2.0150	0.0235	0.0978	0.0210	2.0151	0.0235	0.1038	0.0220	2.0175	0.0241	0.4602
PW91	0.0241	2.0124	0.0255	0.5673	0.0238	2.0122	0.0304	0.6683	0.0256	2.0131	0.0257	0.3241
B3PW91	0.0225	2.0152	0.0253	0.1029	0.0225	2.0155	0.0248	0.1040	0.0229	2.0180	0.0255	0.5080
PBE	0.0232	2.0118	0.0248	0.3365	0.0231	2.0118	0.0250	0.5835	0.0244	2.0130	0.0251	0.2936
PBE0	0.0215	2.0166	0.0262	0.1027	0.0214	2.0166	0.0262	0.0998	0.0232	2.0189	0.0270	0.3925
PBE50	0.0215	2.0209	0.0298	0.4880	0.0215	2.0211	0.0309	0.1758	0.0233	2.0239	0.0314	0.0698
ωPBEh	0.0210	2.0161	0.0257	0.2131	0.0209	2.0162	0.0258	0.1910	0.0223	2.0186	0.0264	0.0975

TABLE IV. $\langle S^2 \rangle$ values for three diradicals (unpaired electrons on opposite centers) derived by the ring opening of cyclohexane and methylcyclohexane.

	rC6r				rC6Cr				rC6rC			
	$^1A_1$	$^3B_1$	$^1B_1$	$^1A_1$	$^3A_1$	$^1A_1$	$^1A_1$	$^1A_1$	$^1A_1$	$^3A_1$	$^1A_1$	$^1A_1$
C-5050	0.0179	2.0238	0.1440	0.1471	1.0254	1.0164	0.1963	0.1770	0.0417	2.0029	0.1830	0.3373
C-PBE50	0.0204	2.0266	0.1665	0.1703	1.0361	1.0111	0.2387	0.2099	0.5829	1.4670	0.2005	0.4048
LDA	0.0084	2.0130	0.0150	0.0148	1.9809	0.0406	0.0160	0.0164	0.0088	2.0123	0.0160	0.0169
BLYP	0.0113	2.0137	0.0231	0.0228	1.2298	0.7957	0.0251	0.0250	0.2395	1.7854	0.0258	0.0265
B3LYP	0.0135	2.0193	0.0477	0.0471	1.1031	0.9291	0.0549	0.0537	0.4476	1.5860	0.0599	0.0685
NC-5050	0.0184	2.0280	0.1498	0.1616	1.0489	0.9977	0.2111	0.1866	0.5162	1.5331	0.1883	0.3633
BHHLYP	0.0185	2.0277	0.1530	0.1662	1.0401	1.0059	0.2204	0.1895	0.5914	1.4577	0.1910	0.3620
B97	0.0162	2.0230	0.0530	0.0526	1.0265	1.0124	0.0605	0.0592	0.6959	1.3446	0.0636	0.0674
ωB97	0.0205	2.0262	0.7805	0.5610	1.0518	0.9954	0.3914	0.5552	0.9082	1.1434	0.6589	0.9785
ωB97X	0.0191	2.0259	0.2687	0.4007	1.0380	1.0083	0.5325	0.5235	1.2006	1.6000	0.5530	0.9015
BP86	0.0127	2.0177	0.0259	0.0256	1.1320	0.8993	0.0278	0.0283	0.0773	1.9530	0.0286	0.0304
B3P86	0.0155	2.0232	0.0513	0.0505	1.0646	0.9738	0.0581	0.0578	0.0767	1.9651	0.0635	0.0741
PW91	0.0137	2.0191	0.0284	0.0281	0.8808	1.1520	0.0309	0.0310	0.3343	1.6982	0.0317	0.0326
B3PW91	0.0161	2.0242	0.0528	0.0519	1.0702	0.9705	0.0596	0.0595	0.0559	1.9851	0.0655	0.0776
PBE	0.0135	2.0188	0.0274	0.0271	1.2057	0.8268	0.0298	0.0300	0.2851	1.7469	0.0305	0.0320
PBE0	0.0178	2.0266	0.0648	0.0636	1.1568	0.8876	0.0751	0.0740	0.3294	1.7154	0.0831	0.1015
PBE50	0.0225	2.0346	0.1990	0.2255	1.8285	0.2287	0.3118	0.2540	0.1590	1.9000	0.2173	0.4863
ωPBEh	0.0168	2.0257	0.4910	0.2686	1.0648	0.9794	0.4172	0.3459	0.4532	1.5914	0.2129	0.6076

TABLE V. $\langle S^2 \rangle$ values for TMM.

	TMM			
	$^3B_1$	$^1B_1$	$^1A_1$	$^1A_1$
C-5050	2.1577	0.6249	0.1518	0.0826
C-PBE50	2.1766	0.4538	0.1620	0.0915
LDA	2.0253	0.0487	0.0281	0.0108
BLYP	2.0354	0.8404	0.0362	0.0201
B3LYP	2.0766	0.6550	0.0739	0.0391
NC-5050	2.1657	0.6912	0.1607	0.0826
BHHLYP	2.1665	0.5149	0.1597	0.0841
B97	2.0764	0.6077	0.0748	0.0396
ωB97	2.1421	0.2557	0.1583	0.0838
ωB97X	2.1429	0.3265	0.1396	0.0732
BP86	2.0447	0.6202	0.0432	0.0221
B3P86	2.0906	0.0643	0.0903	0.0419
PW91	2.0448	0.6869	0.0434	0.0235
B3PW91	2.0945	0.0616	0.0948	0.0437
PBE	2.0459	0.6820	0.0433	0.0228
PBE0	2.1100	0.0925	0.1090	0.0517
PBE50	2.1887	0.9033	0.1886	0.0916
ωPBEh	2.1308	0.3795	0.1300	0.0589

TABLE VI. $\langle S^2 \rangle$ values for $\sigma\sigma$, $\sigma\pi$ and $\pi\pi$ diradicals.

	o-benzyne		m-benzyne		p-benzyne		α,2-didehydrotoluene		α,3-didehydrotoluene		α,4-didehydrotoluene		m-xylylene		
	$^1A_1$	$^3B_2$	$^1A_1$	$^3B_2$	^1A_g	$^3B_{1u}$	$^3B_2$	$^1A_1$	$^3B_2$	$^1A_1$	$^3B_2$	$^1A_1$	$^3B_2$	$^1A_1$	$^1B_2$
C-5050	0.0235	2.0216	0.0532	2.0821	0.0223	2.0184	2.2589	0.1527	1.5535	0.5974	2.2516	0.1460	2.3916	0.2153	0.3325
C-PBE50	0.0275	2.0235	0.0727	2.1134	0.0267	2.0203	1.9334	0.5836	1.1135	1.1424	1.9509	0.5438	2.4424	0.2369	0.3607
LDA	0.0118	2.0212	0.0175	2.0344	0.0140	2.0160	2.0345	0.0270	2.0149	0.0150	2.0326	0.0268	2.0361	0.0217	0.0346
BLYP	0.0143	2.0053	0.0194	2.0271	0.0174	2.0057	1.4811	0.5345	1.0701	0.9514	1.5157	0.5567	2.0431	0.0295	0.0393
B3LYP	0.0174	2.0098	0.0280	2.0447	0.0198	2.0155	1.7618	0.4211	1.0822	1.0012	1.7837	0.3844	2.1529	0.0791	0.1207
NC-5050	0.0229	2.0253	0.0531	2.0920	0.0235	2.0221	2.2603	0.1623	1.5557	0.7060	2.2627	0.1482	2.4058	0.2260	0.3539
BHHLYP	0.0233	2.0236	0.0532	2.0903	0.0235	2.0210	2.2650	0.1859	1.6315	0.1897	2.2486	0.1839	2.4120	0.2282	0.3559
B97	0.0193	2.0210	0.0326	2.0561	0.0272	2.0185	1.6765	0.5161	1.0696	1.0129	1.6574	0.5256	2.1462	0.0773	0.1182
ωB97	0.0693	2.0097	0.0530	2.0757	0.0276	2.0207	1.8333	0.3769	1.4315	1.1350	1.7115	0.7216	2.4220	0.2324	0.3856
ωB97X	0.0264	2.0208	0.0484	2.0745	0.0387	2.0199	1.7624	0.6090	1.2281	1.1108	1.6685	0.7055	2.3543	0.1907	0.3295
BP86	0.0156	2.0202	0.0224	2.0406	0.0195	2.0173	1.9228	0.1764	1.1432	0.8522	1.9497	0.1644	2.0662	0.0378	0.0655
B3P86	0.0185	2.0255	0.0320	2.0588	0.0225	2.0213	2.1203	0.0722	1.1886	0.8879	2.1180	0.0673	2.1756	0.0942	0.1456
PW91	0.0167	2.0213	0.0244	2.0436	0.0213	2.0171	1.8217	0.2930	1.1327	0.9160	1.8476	0.2429	2.0709	0.0386	0.0657
B3PW91	0.0195	2.0274	0.0345	2.0662	0.0236	2.0229	2.1286	0.0769	1.2025	0.9799	2.1246	0.0718	2.1838	0.0985	0.1594
PBE	0.0165	2.0212	0.0237	2.0421	0.0204	2.0172	1.8387	0.2660	1.1426	0.9097	1.8755	0.2137	2.0692	0.0378	0.0670
PBE0	0.0210	2.0276	0.0389	2.0738	0.0250	2.0237	2.1532	0.0944	1.2800	0.8956	2.1474	0.0888	2.2255	0.1205	0.1876
PBE50	0.0254	2.0354	0.0700	2.1379	0.0294	2.0293	2.0272	0.4991	1.2969	0.9743	2.0624	0.4439	2.4671	0.2665	0.4035
ωPBE	0.0278	2.0202	0.0412	2.0629	0.0252	2.0234	2.1693	0.1432	1.2940	0.8921	2.1742	0.1236	2.2999	0.1620	0.2634

II. CARTESIAN GEOMETRIES

A. CH_2

Geometry and nuclear repulsion energy: C.D. Sherrill, M.L. Leininger, T.J. Van Huis, and H.F. Schaefer; J. Chem. Phys. 108, 1040 (1998); Level of theory: FCI/TZ2P.

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3B1
rCH = 1.0775
HCH = 133.29
Enu = 6.1608618178 hartree
1A1
rCH = 1.1089
HCH = 101.89
Enu = 6.0337753316 hartree
1B1
rCH = 1.0748
HCH = 141.56
Enu = 6.1688997427 hartree
1A1
rCH = 1.0678
HCH = 170.08
Enu = 6.1956449370 hartree
```

SF-CCSD(dT) calculations: aug-cc-pVQZ, UHF, no frozen core.

B. NH_2^+

Geometry and nuclear repulsion energy: J.C. Stefens, Y. Yamaguchi, C.D. Sherrill, and H.F. Schaefer, J. Phys. Chem. 102, 3999 (1998). Level of theory: CISD/TZ2P(f,d).

```
3B1
rNH = 1.0295
HNH = 150.88
Enu = 7.4617278181 hartree
1A1
rNH = 1.0459
HNH = 107.96
Enu = 7.3961310239 hartree
1B1
rNH = 1.0293
HNH = 161.47
Enu = 7.4580461860 hartree
1A1
rNH = 1.0315
HNH = 180.0
Enu = 7.4387489642 hartree
```

SF-CCSD(dT) calculation: aug-cc-pVQZ, UHF, no frozen core.

C. SiH_2

Geometry and nuclear repulsion energy: Y. Yamaguchi, T.J. Van Huis, C.D. Sherrill, and H.F. Schaefer, Theor. Chem. Acc. 97, 341 (1997). Level of theory: CISD/TZ2P(f,d).

```
1A1
rSiH = 1.5145
HSiH = 92.68
Enu  = 10.0248887208 hartree
3B1
rSiH = 1.4770
HSiH = 118.26
Enu  = 10.2405012513 hartree
1B1
rSiH = 1.4830
HSiH = 122.65
Enu  = 10.1945630475 hartree
1A1
rSiH = 1.4573
HSiH = 162.34
Enu  = 10.3511452589 hartree
```

SF-CCSD(dT) calculation: aug-cc-pVQZ, UHF, no frozen core.

D. PH_2^+

Geometry and nuclear repulsion energy: T.J. Van Huis, Y. Yamaguchi, C.D. Sherrill, and H. F. Schaefer, J. Phys. Chem. 101, 6955 (1997). Level of theory: CISD/TZ2P(f,d).

```
1A1
rPH = 1.4178
HPH = 93.06
Enu = 11.4542930384 hartree
3B1
rPH = 1.4056
HPH = 121.77
Enu = 11.5097981933 hartree
1B1
rPH = 1.4194
HPH = 124.84
Enu = 11.3948330304 hartree
1A1
rPH = 1.4118
HPH = 159.62
Enu = 11.4351503777 hartree
```

SF-CCSD(dT) calculation: aug-cc-pVQZ, FROZEN_CORE, UHF.

E. C6rr

Geometry and nuclear repulsion energy: Enoch Dames, private communication. Level of theory: UB3LYP/6-311G(2d,p).

```
SINGLET
C  2.053170 -0.395273 -0.123362
C  3.301054  0.262168  0.216251
C  0.787227  0.464463 -0.104113
C -0.509961 -0.339459  0.003423
C -1.769925  0.527460 -0.036160
C -3.062892 -0.280220  0.081300
H -3.942115  0.367234  0.049518
H -3.152778 -1.002274 -0.735028
H -3.096618 -0.839086  1.020571
H -1.724785  1.266387  0.771736
H -1.782221  1.101449 -0.969406
H -0.553738 -1.076826 -0.808091
H -0.500326 -0.919129  0.935429
H  0.871155  1.175544  0.721757
H  0.772038  1.060662 -1.023073
H  2.047073 -1.157827 -0.929944
H  2.120028 -0.987293  0.813197
H  4.111134 -0.435485 -0.079937
Enu = 226.4557391679 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, UHF.

F. rC6r

Geometry and nuclear repulsion energy: this work. Level of theory: UB3LYP/6-311G(d,p).

For this system, there was a problem with optimizing the singlet state; thus, we used triplet geometry instead. The singlet and triplet states are almost exactly degenerate.

```
Triplet!!!
C  3.485147 -0.284738 -0.132482
C  2.254839  0.464444 0.245798
C  0.948171 -0.218941 -0.191779
C -0.298466  0.583451  0.196611
C -1.637238  0.013751 -0.324390
C -2.758572  0.966934 -0.067512
H -3.780320  0.615977  0.027755
H  4.402140 -0.183840  0.436306
H -2.599820  2.038966 -0.115542
H  3.537214 -0.826177 -1.071212
C -1.953842 -1.381437  0.237889
H  2.238322  0.631735  1.330428
```

```
H -1.526829 -0.096137 -1.420519
H  2.279235  1.477782 -0.194861
H  0.910639 -1.220774  0.247491
H -0.354149  0.671713  1.289303
H  0.966973 -0.362460 -1.280300
H -0.189132  1.607659 -0.182182
H -2.918009 -1.739636 -0.133870
H -2.006881 -1.358009  1.330922
H -1.199614 -2.117578 -0.048527
Enu = 297.8868862614 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, UHF.

G. C7rr

Geometry and nuclear repulsion energy: Enoch Dames, private communication. Level of theory: UB3LYP/6-311G(2d,p).

```
SINGLET
C  3.918000  0.400806  0.230025
C  2.719960 -0.339937 -0.115719
C  1.404137  0.442157 -0.120008
C  0.156953 -0.436278 -0.002549
C -1.151620  0.354705 -0.052006
C -2.401336 -0.519021  0.076646
C -3.704109  0.279490  0.026121
H -4.576428 -0.372234  0.114273
H -3.752030  1.009336  0.839040
H -3.794644  0.829391 -0.914741
H -2.400535 -1.268880 -0.722942
H -2.353605 -1.080301  1.016515
H -1.150953  1.106351  0.746828
H -1.199127  0.916169 -0.992881
H  0.156781 -1.184691 -0.804987
H  0.201648 -1.002711  0.936305
H  1.440850  1.172287  0.692770
H  1.358087  1.019490 -1.049826
H  2.769126 -1.114447 -0.909328
H  2.812841 -0.908244  0.833228
H  4.776307 -0.244819 -0.047345
Enu = 288.7822823391 hartree
```

SF-CCSD(dT) calculations: 6-311G(d), FROZEN_CORE, UHF.

H. C6rrC

Geometry and nuclear repulsion energy: Enoch Dames, private communication. Level of theory: UB3LYP/6-311G(2d,p).

```
SINGLET
C 3.832273  -0.311113 -0.010474
C 2.633517   0.364653  0.510976
C 1.392858  -0.308606  0.119546
C 0.104843   0.518174  0.130877
C -1.164845 -0.324313 -0.000968
C -2.449050  0.507543 -0.008368
C -3.716329 -0.338145 -0.137744
H -2.498695  1.101102  0.911113
H -2.405500  1.229946 -0.831423
H -3.712875 -0.917362 -1.065248
H -3.805241 -1.045392  0.691574
H -4.613776  0.284712 -0.139484
H -1.116561 -0.920635 -0.920593
H -1.207302 -1.047546  0.823721
H  0.080413  1.105721  1.052557
H  0.148782  1.242634 -0.689947
H  1.463336 -0.957498 -0.774068
H  1.372009 -1.023990  0.975349
H  4.040515  0.318461 -0.896771
H  4.712840 -0.199653  0.625556
H  3.724940 -1.348035 -0.371187
Enu = 287.5587886365 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, UHF.

I. rC6Cr

Geometry and nuclear repulsion energy: Enoch Dames, private communication. Level of theory: UB3LYP/6-311G(2d,p).

```
SINGLET
C -3.250244 -0.832024  0.10728
C -1.829261 -0.479995 -0.334695
C -1.321049  0.828450  0.277768
C  0.080311  1.242910 -0.191456
C  1.206423  0.339951  0.265072
C  2.295403 -0.006966 -0.534121
C  3.372645 -0.771639  0.179650
H  3.147978 -1.084519  1.213605
H  4.236044 -0.097125  0.217584
H  3.707140 -1.636481 -0.397153
H  1.197069  0.117031  1.349271
H  0.308507  2.238381  0.206421
H  0.125051  1.327091 -1.280514
H -1.332811  0.747485  1.371460
H -2.022021  1.631634  0.028145
H -1.792670 -0.404429 -1.427078
```

```
H -1.158198 -1.303180 -0.065209
H -3.588163 -1.768308 -0.342264
H -3.958245 -0.050353 -0.181489
H -3.309147 -0.944934  1.193317
H  1.126858 -0.669703 -0.482144
Enu = 294.3742946065 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, UHF.

J. rC7r

Geometry and nuclear repulsion energy: this work. Level of theory: UB3LYP/6-311G(2d,p).

```
SINGLET
C  3.766594 -0.078584  0.193126
C  2.437584 -0.499950 -0.322848
C  1.265880  0.355498  0.221346
C -0.096507 -0.081595 -0.321461
C -1.264520  0.782624  0.215173
C -2.600161  0.394226 -0.320684
C -3.391503 -0.726794  0.256780
H -3.070131 -1.710420 -0.123286
H -3.289891 -0.769150  1.346307
H -4.454714 -0.638475  0.018100
H -2.896511  0.785611 -1.288882
H -1.054090  1.829914 -0.030702
H -1.267629  0.712599  1.310325
H -0.274950 -1.130614 -0.061983
H -0.089514 -0.031779 -1.415874
H  1.442738  1.405892 -0.033366
H  1.262493  0.301511  1.315272
H  4.302714  0.744466 -0.262848
H  4.154050 -0.472308  1.124270
H  2.422157 -0.439448 -1.417187
H  2.247755 -1.547541 -0.063807
Enu = 289.2390610955 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, UHF.

K. TMM

Geometry and nuclear repulsion energy: L.V. Slipchenko and A.I. Krylov, J. Chem. Phys. 117, 4694 (2002). Level of theory: SF-TDDFT(50/50)/6-31G(d).

```
3A2
C  0.000000  0.000000 0.000000
C  1.402100  0.000000 0.000000
```

```
C -0.701050  1.214254 0.000000
C -0.701050 -1.214254 0.000000
H  1.958596  0.920333 0.000000
H  1.958596 -0.920333 0.000000
H -0.182266  2.156360 0.000000
H -1.776330  1.236027 0.000000
H -0.182266 -2.156360 0.000000
H -1.776330 -1.236027 0.000000
Enu = 106.2360784394 hartree
1B1
C  0.000000  0.000000  0.037396
C  0.000000  0.000000 -1.444404
C  1.199540  0.000000  0.708071
C -1.199540  0.000000  0.708071
H  0.000000 -0.923986 -1.996960
H  0.000000  0.923986 -1.996960
H  2.138484  0.000000  0.184817
H  1.229990  0.000000  1.784740
H -2.138484  0.000000  0.184817
H -1.229990  0.000000  1.784740
Enu = 105.6919955295 hartree
1A1
C  0.000000 0.000000  0.040626
C  0.000000 0.000000  1.379026
C -1.246425 0.000000 -0.705344
C  1.246425 0.000000 -0.705344
H -0.918156 0.000000  1.942555
H  0.918156 0.000000  1.942555
H -2.189011 0.000000 -0.189721
H -1.252801 0.000000 -1.779725
H  2.189011 0.000000 -0.189721
H  1.252801 0.000000 -1.779725
Enu = 105.6085150023 hartree
2 1A1
C  0.000000  0.000000 0.000000
C  1.392500  0.000000 0.000000
C -0.696250  1.205940 0.000000
C -0.696250 -1.205940 0.000000
H  1.949327  0.919431 0.000000
H  1.949327 -0.919431 0.000000
H -0.178413  2.147882 0.000000
H -1.770914  1.228451 0.000000
H -0.178413 -2.147882 0.000000
H -1.770914 -1.228451 0.000000
Enu = 106.8018704598 hartree
```

SF-CCSD(dT) calculation: cc-pVQZ, FROZEN_CORE, UHF.

L. ortho-benzyne

Geometry and nuclear repulsion energy: S.V. Levchenko and A.I. Krylov, J. Chem. Phys. 117, 4694 (2002). Level of theory: SF-TDDFT(50/50)/6-311G(d).

```
1A1
H  2.518466  0.000000 -0.131102
C  1.443350  0.000000 -0.129071
C  0.698800  0.00000   1.050271
H  1.218994  0.000000  1.994214
C -0.698800  0.000000  1.050271
H -1.218994  0.000000  1.994214
C -1.443350  0.000000 -0.129071
H -2.518466  0.000000 -0.131102
C -0.620604  0.000000 -1.229469
C  0.620604  0.000000 -1.229469
Enu = 189.1020524482 hartree
3B2
H  2.476058 0.000000  -0.120773
C  1.397826 0.000000  -0.115266
C  0.690428 0.00000    1.085671
H  1.229929 0.000000   2.017939
C -0.690428 0.000000   1.085671
H -1.229929 0.000000   2.017939
C -1.397826 0.000000  -0.115266
H -2.476058 0.000000  -0.120773
C -0.692326 0.000000  -1.284303
C  0.692326 0.000000  -1.284303
Enu = 189.1020524482 hartree
```

Level of theory: SF-CCSD/cc-pVTZ (this work).

```
1A1
H  2.468243 0.000000 -0.099328
C  1.383742 0.000000 -0.126152
C  0.681490 0.000000  1.141646
H  1.241496 0.000000  2.066368
C -0.681490 0.000000  1.141646
H -1.241496 0.000000  2.066368
C -1.383742 0.000000 -0.126152
H -2.468243 0.000000 -0.099328
C -0.667458 0.000000 -1.343335
C  0.667458 0.000000 -1.343335
Enu = 184.0328760159 hartree
3B2
H  2.488408 0.000000 -0.120332
C  1.406907 0.000000 -0.115084
C  0.694928 0.000000  1.092458
H  1.235563 0.000000  2.028479
```

```
C -0.694928 0.000000  1.092458
H -1.235563 0.000000  2.028479
C -1.406907 0.000000 -0.115084
H -2.488408 0.000000 -0.120332
C -0.697717 0.000000 -1.295397
C  0.697717 0.000000 -1.295397
Enu = 185.5422070217 hartree
```

Level of theory: NC-SF-TDDFT/LDA/cc-pVTZ (this work).

```
3B2
H  2.487876 0.000000 -0.125955
C  1.389767 0.000000 -0.116940
C  0.691597 0.000000  1.090307
H  1.244378 0.000000  2.033978
C -0.691597 0.000000  1.090307
H -1.244378 0.000000  2.033978
C -1.389767 0.000000 -0.116940
H -2.487876 0.000000 -0.125955
C -0.692733 0.000000 -1.291371
C 0.692733 0.000000  -1.291371
Enu = 186.3396532887 hartree
```

SF-CCSD(dT) calculation: P.U. Manohar and A.I. Krylov, J. Chem. Phys. 129, 194105 (2008). cc-pVTZ.

M. meta-benzyne

Geometry and nuclear repulsion energy: S.V. Levchenko and A.I. Krylov, J. Chem. Phys. 117, 4694 (2002). Level of theory: SF-TDDFT(50/50)/6-311G(d).

```
1A1
H -2.14490 0.000000 -1.09181
C -1.16532 0.000000 -0.64614
C  0.00000 0.000000 -1.40225
H  0.00000 0.000000 -2.48201
C  1.16532 0.000000 -0.64614
H  2.14490 0.000000 -1.09181
C  1.00834 0.000000  0.70681
C -0.00000 0.000000  1.60963
H  0.00000 0.000000  2.68230
C -1.00834 0.000000  0.70681
Enu = 188.8101975912 hartree
3B2
H -2.14689 0.000000  1.16892
C -1.21423 0.000000  0.63214
C  0.00000 0.000000  1.31213
H  0.00000 0.000000  2.39042
```

```
C  1.21423 0.000000  0.63214
H  2.14689 0.000000  1.16892
C  1.15425 0.000000 -0.73302
C  0.00000 0.000000 -1.47122
H  0.00000 0.000000 -2.54931
C -1.15425 0.000000 -0.73302
Enu = 187.2036581675 hartree
```

Level of theory: SF-CCSD/cc-pVTZ (this work).

```
1A1
H -2.151817 0.000000 -1.099068
C -1.170975 0.000000 -0.647998
C  0.000000 0.000000 -1.400845
H  0.000000 0.000000 -2.484759
C  1.170975 0.000000 -0.647998
H  2.151817 0.000000 -1.099068
C  1.030415 0.000000  0.713177
C  0.000000 0.000000  1.604436
H  0.000000 0.000000  2.679188
C -1.030415 0.000000  0.713177
Enu = 187.8622985704 hartree
3B2
H -2.153500 0.000000  1.173398
C -1.217705 0.000000  0.635094
C  0.000000 0.000000  1.316881
H  0.000000 0.000000  2.398886
C  1.217705 0.000000  0.635094
H  2.153500 0.000000  1.173398
C  1.160250 0.000000 -0.737064
C  0.000000 0.000000 -1.477482
H  0.000000 0.000000 -2.558454
C -1.160250 0.000000 -0.737064
Enu = 186.4551109530 hartree
```

Level of theory: NC-SF-TDDFT/LDA/cc-pVTZ (this work).

```
1A1
H -2.144900 0.000000 -1.091535
C -1.165320 0.000000 -0.645865
C  0.000000 0.000000 -1.401975
H  0.000000 0.000000 -2.481735
C  1.165320 0.000000 -0.645865
H  2.144900 0.000000 -1.091535
C  1.008340 0.000000  0.707085
C  0.000000 0.000000  1.609905
H  0.000000 0.000000  2.682575
C -1.008340 0.000000  0.707085
Enu = 188.8101975912 hartree
```

```
3B2
H -2.146890 0.000000  1.168574
C -1.214230 0.000000  0.631794
C  0.000000 0.000000  1.311784
H  0.000000 0.000000  2.390074
C  1.214230 0.000000  0.631794
H  2.146890 0.000000  1.168574
C  1.154250 0.000000 -0.733366
C  0.000000 0.000000 -1.471566
H  0.000000 0.000000 -2.549656
C -1.154250 0.000000 -0.733366
Enu = 187.2036581675 hartree
```

SF-CCSD(dT) calculation: P.U. Manohar and A.I. Krylov, J. Chem. Phys. 129, 194105 (2008). cc-pVTZ.

N. para-benzyne

Geometry and nuclear repulsion energy: S.V. Levchenko and A.I. Krylov, J. Chem. Phys. 117, 4694 (2002). Level of theory: SF-TDDFT(50/50)/6-311G(d).

```
1A1
H  2.145810 -1.225292 0.000000
C  1.201382 -0.709285 0.000000
C  1.201382  0.709285 0.000000
H  2.145810  1.225292 0.000000
C  0.000000  1.335664 0.000000
C -1.201382  0.709285 0.000000
H -2.145810  1.225291 0.000000
C -1.201382 -0.709285 0.000000
H -2.145810 -1.225291 0.000000
C  0.000000 -1.335664 0.000000
Enu = 187.2138176166 hartree
3B2
H  2.144994 -1.255165 0.000000
C  1.222802 -0.697850 0.000000
C  1.222802  0.697850 0.000000
H  2.144994  1.255165 0.000000
C  0.000000  1.308815 0.000000
C -1.222802  0.697850 0.000000
H -2.144994  1.255165 0.000000
C -1.222802 -0.697850 0.000000
H -2.144994 -1.255165 0.000000
C  0.000000 -1.308815 0.000000
Enu = 187.1095116544 hartree
```

Level of theory: SF-CCSD/cc-pVTZ (this work).

```
1A1
H  2.157047  1.233655 0.000000
C  1.211871  0.711141 0.000000
C  1.211871 -0.711141 0.000000
H  2.157047 -1.233655 0.000000
C  0.000000 -1.347072 0.000000
C -1.211871 -0.711141 0.000000
H -2.157047 -1.233655 0.000000
C -1.211871  0.711141 0.000000
H -2.157047  1.233655 0.000000
C  0.000000  1.347072 0.000000
Enu = 185.8857438812 hartree
3B2
H  2.155804 -1.261577 0.000000
C  1.231260 -0.701634 0.000000
C  1.231260  0.701634 0.000000
H  2.155804  1.261577 0.000000
C  0.000000  1.321097 0.000000
C -1.231260  0.701634 0.000000
H -2.155804  1.261577 0.000000
C -1.231260 -0.701634 0.000000
H -2.155804 -1.261577 0.000000
C  0.000000 -1.321097 0.000000
Enu = 185.8292899796 hartree
```

Level of theory: NC-SF-TDDFT/LDA/cc-pVTZ (this work).

```
1A1
H  2.145810  1.225292 0.000000
C  1.201382  0.709285 0.000000
C  1.201382 -0.709285 0.000000
H  2.145810 -1.225292 0.000000
C  0.000000 -1.335664 0.000000
C -1.201382 -0.709285 0.000000
H -2.145810 -1.225291 0.000000
C -1.201382  0.709285 0.000000
H -2.145810  1.225291 0.000000
C  0.000000  1.335664 0.000000
Enu = 187.2138176166
3B2
H  2.144994 -1.255165 0.000000
C  1.222802 -0.697850 0.000000
C  1.222802  0.697850 0.000000
H  2.144994  1.255165 0.000000
C  0.000000  1.308815 0.000000
C -1.222802  0.697850 0.000000
H -2.144994  1.255165 0.000000
C -1.222802 -0.697850 0.000000
```

```
H -2.144994 -1.255165 0.000000
C  0.000000 -1.308815 0.000000
Enu = 187.1095116544
```

SF-CCSD(dT) calculation: P.U. Manohar and A.I. Krylov, J. Chem. Phys. 129, 194105, (2008). cc-pVTZ.

O. alpha,2-didehydrotoluene

Geometry and nuclear repulsion energy: this work. Level of theory: SF-TDDFT(50/50)/6-311G(d).

```
TRIPLET
C  1.020471  0.077237 0.000
C  0.198938  1.202122 0.000
C  0.308312 -1.151038 0.000
C -1.156060  1.223411 0.000
C -1.063921 -1.182044 0.000
C -1.808786 -0.008282 0.000
C  2.414372  0.138304 0.000
H  3.005794 -0.758865 0.000
H  2.923769  1.083051 0.000
H  0.870643 -2.071165 0.000
H -1.712634  2.145601 0.000
H -1.571687 -2.131810 0.000
H -2.885238 -0.046149 0.000
Enu = 251.6295479028 hartree
SINGLET
C  1.013998  0.074033 0.000
C  0.193208  1.199114 0.000
C  0.308282 -1.145750 0.000
C -1.154702  1.222553 0.000
C -1.072316 -1.180917 0.000
C -1.812506 -0.015889 0.000
C  2.418804  0.140525 0.000
H  3.012342 -0.754788 0.000
H  2.923576  1.087046 0.000
H  0.870601 -2.065974 0.000
H -1.711842  2.144559 0.000
H -1.576026 -2.132747 0.000
H -2.889007 -0.050359 0.000
Enu = 251.6475045480 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, ROHF.

P. alpha,3-didehydrotoluene

Geometry and nuclear repulsion energy: this work. Level of theory: SF-TDDFT(50/50)/6-311G(d).

```
TRIPLET
C  0.956088  0.018188 0.0000
C  0.127954  1.162360 0.0000
C  0.317315 -1.249671 0.0000
C -1.241571  1.063962 0.0000
C -1.035725 -1.269534 0.0000
C -1.866969 -0.183724 0.0000
C  2.347958  0.126446 0.0000
H  2.974177 -0.746495 0.0000
H  2.829666  1.086951 0.0000
H  0.591998  2.134433 0.0000
H  0.909022 -2.150114 0.0000
H -1.843133  1.958313 0.0000
H -2.939440 -0.271780 0.0000
Enu = 252.4222171565 hartree
SINGLET
C  0.958368  0.018945 0.000
C  0.127057  1.164542 0.000
C  0.317561 -1.250746 0.000
C -1.242636  1.064638 0.000
C -1.034923 -1.270715 0.000
C -1.868452 -0.184970 0.000
C  2.347950  0.126616 0.000
H  2.975441 -0.746008 0.000
H  2.831252  1.086855 0.000
H  0.590726  2.136859 0.000
H  0.910371 -2.150775 0.000
H -1.845146  1.958407 0.000
H -2.940976 -0.273252 0.000
Enu = 252.2599737842 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, ROHF.

Q. alpha,4-didehydrotoluene

Geometry and nuclear repulsion energy: this work. Level of theory: SF-TDDFT(50/50)/6-311G(d).

```
TRIPLET
C  0.898362 -0.000006 0.000
C  0.169069  1.210363 0.000
C  0.169060 -1.210369 0.000
C -1.209377  1.216892 0.000
```

```
C -1.209387 -1.216888 0.000
C -1.838280  0.000005 0.000
C  2.294983 -0.000002 0.000
H  2.852158 -0.918638 0.000
H  2.852144  0.918645 0.000
H  0.707215  2.144769 0.000
H  0.707197 -2.144781 0.000
H -1.757644  2.143768 0.000
H -1.757666 -2.143758 0.000
Enu = 252.5546911819 hartree
SINGLET
C  0.892817 -0.000013 0.0000
C  0.170345  1.206724 0.0000
C  0.170320 -1.206735 0.0000
C -1.216861  1.216035 0.0000
C -1.216888 -1.216015 0.0000
C -1.841085  0.000017 0.0000
C  2.308817 -0.000010 0.0000
H  2.862918 -0.920736 0.0000
H  2.862901  0.920727 0.0000
H  0.708385  2.141945 0.0000
H  0.708334 -2.141971 0.0000
H -1.763239  2.144743 0.0000
H -1.763287 -2.144712 0.0000
Enu = 252.1767914962 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, ROHF.

R. meta-xylylene

Geometry and nuclear repulsion energy: T. Wang and A. I. Krylov, J. Chem. Phys. 123, 104304 (2005). Level of theory: 3B2: UHF-CCSD/6-31G(d). 1A1 and 1B2: UHF-EOM-SF-CCSD/631G(d).

```
3B1
C  1.242069  0.338082 0.000000
C  0.000308  1.024806 0.000000
C -1.241301  0.337807 0.000000
C -1.212383 -1.094901 0.000000
C -0.001370 -1.781278 0.000000
C  1.210687 -1.096748 0.000000
C  2.459320  1.033715 0.000000
C -2.457377  1.035491 0.000000
H  0.000187  2.114806 0.000000
H -2.153995 -1.641972 0.000000
H -0.002200 -2.870277 0.000000
H  2.151464 -1.645253 0.000000
H  2.488778  2.120315 0.000000
```

```
H  3.410464  0.507507 0.000000
H -2.485004  2.122140 0.000000
H -3.409407  0.510889 0.000000
Enu = 320.8689838538 hartree
1A1
C  1.223027  0.320433 0.000000
C  0.000165  1.002056 0.000000
C -1.222346  0.319805 0.000000
C -1.206081 -1.082101 0.000000
C -0.001180 -1.773140 0.000000
C  1.205772 -1.085691 0.000000
C  2.481799  1.044171 0.000000
C -2.480634  1.044384 0.000000
H -0.000115  2.093056 0.000000
H -2.148567 -1.627666 0.000000
H -0.002801 -2.862139 0.000000
H  2.146630 -1.634059 0.000000
H  2.500810  2.130004 0.000000
H  3.430688  0.515960 0.000000
H -2.500814  2.130196 0.000000
H -3.428954  0.515152 0.000000
Enu = 321.3313811081 hartree
1B2
C  1.265839  0.368759 0.000000
C  0.000065  1.065782 0.000000
C -1.265471  0.368328 0.000000
C -1.211918 -1.120710 0.000000
C -0.000745 -1.790423 0.000000
C  1.211367 -1.122411 0.000000
C  2.442112  1.020991 0.000000
C -2.441377  1.021222 0.000000
H -0.000121  2.154782 0.000000
H -2.153585 -1.665692 0.000000
H -0.001510 -2.880423 0.000000
H  2.152269 -1.668716 0.000000
H  2.493213  2.107791 0.000000
H  3.389133  0.485366 0.000000
H -2.488071  2.108220 0.000000
H -3.390562  0.489440 0.000000
Enu = 319.6820870636 hartree
```

SF-CCSD(dT) calculation: 6-311G(d), FROZEN_CORE, ROHF.