Supplementary Material for "Can GW Handle Multireference Systems?"

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I. BE + H_2 REACTION

- PYSCF format of the Be(3s2p)/H(2s) basis set:

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BASIS "ao basis" SPHERICAL PRINT
#BASIS SET: (4s) -> [2s]
H   S
          19.24060E+00          0.032828E+00
          2.899200E+00          0.231208E+00
          0.653400E+00          0.817238E+00
H   S
          0.177600E+00          1.000000E+00
#BASIS SET: (10s,3p) -> [3s,2p]
Be  S
          1267.070000E+00       0.001940E+00
           190.356000E+00       0.014786E+00
            43.295900E+00       0.071795E+00
            12.144200E+00       0.236348E+00
             3.809230E+00       0.471763E+00
             1.268470E+00       0.355183E+00
Be  S
             5.693880E+00      -0.028876E+00
             1.555630E+00      -0.177565E+00
             0.171855E+00       1.071630E+00
Be  S
             0.057181E+00       1.000000E+00
Be  P
             5.693880E+00       1.000000E+00
Be  P
             1.555630E+00       0.144045E+00
             0.171855E+00       0.949692E+00
END
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TABLE I. Hartree-Fock (HF) ground-state energy and the first four roots of the FCI matrix (in E_h) for the cationic state of BeH_2 as functions of x (in a_0).

		FCI energies			
x	HF energy	Root #1	Root #2	Root #3	Root #4
0.00	−15.263651	−15.382085	−15.325298	−15.085238	−15.085238
0.25	−15.252976	−15.371673	−15.313744	−15.114749	−15.070233
0.50	−15.237634	−15.361208	−15.298337	−15.106722	−15.060838
0.75	−15.291210	−15.353711	−15.281222	−15.106733	−15.059047
1.00	−15.291011	−15.351717	−15.264931	−15.117632	−15.065947
1.25	−15.297507	−15.355837	−15.250765	−15.140054	−15.080525
1.50	−15.308517	−15.364227	−15.238656	−15.171047	−15.099709
1.75	−15.319927	−15.373332	−15.232856	−15.200120	−15.119700
2.00	−15.327584	−15.379481	−15.257115	−15.197410	−15.179439
2.25	−15.328808	−15.380229	−15.292627	−15.207700	−15.177748
2.50	−15.322599	−15.374630	−15.326788	−15.232365	−15.164957
2.75	−15.290361	−15.363071	−15.357741	−15.253019	−15.176695
3.00	−15.323047	−15.385155	−15.347455	−15.269897	−15.185796
3.25	−15.351455	−15.409104	−15.331626	−15.283449	−15.185619
3.50	−15.375619	−15.429384	−15.320125	−15.293772	−15.216857
3.75	−15.394136	−15.444428	−15.313115	−15.299627	−15.242929
4.00	−15.402460	−15.449608	−15.303612	−15.296734	−15.256302

TABLE II. Hartree-Fock (HF) ground-state energy and the first four roots of the FCI matrix (in E_h) for the neutral state of BeH_2 as functions of x (in a_0).

		FCI energies			
x	HF energy	Root #1	Root #2	Root #3	Root #4
0.00	−15.741722	−15.799589	−15.544641	−15.544641	−15.428489
0.25	−15.737372	−15.794413	−15.537486	−15.534788	−15.425578
0.50	−15.727543	−15.784419	−15.535823	−15.525383	−15.427798
0.75	−15.714324	−15.771594	−15.540840	−15.519058	−15.431159
1.00	−15.699912	−15.757968	−15.552790	−15.517841	−15.435575
1.25	−15.685357	−15.744499	−15.570455	−15.522037	−15.440696
1.50	−15.670004	−15.730657	−15.591041	−15.529868	−15.445519
1.75	−15.651879	−15.714843	−15.610952	−15.538174	−15.450125
2.00	−15.628721	−15.695276	−15.626955	−15.543742	−15.464346
2.25	−15.599090	−15.671020	−15.636897	−15.544303	−15.502656
2.50	−15.562872	−15.643185	−15.639669	−15.545961	−15.538651
2.75	−15.488827	−15.635005	−15.623459	−15.575084	−15.419795
3.00	−15.536692	−15.645844	−15.623322	−15.555947	−15.441077
3.25	−15.580201	−15.680902	−15.605617	−15.519404	−15.460020
3.50	−15.618799	−15.714004	−15.583496	−15.482298	−15.476641
3.75	−15.650408	−15.741386	−15.559087	−15.489482	−15.463372
4.00	−15.669900	−15.757444	−15.533429	−15.493812	−15.474227

TABLE III. Hartree-Fock (HF) ground-state energy and the first four roots of the FCI matrix (in E_h) for the anionic state of BeH_2 as functions of x (in a_0).

		FCI energies			
x	HF energy	Root #1	Root #2	Root #3	Root #4
0.00	−15.603945	−15.665746	−15.665745	−15.637509	−15.488977
0.25	−15.609962	−15.669333	−15.658440	−15.618335	−15.466462
0.50	−15.618880	−15.676885	−15.647558	−15.588419	−15.434329
0.75	−15.626063	−15.683328	−15.634960	−15.557903	−15.427763
1.00	−15.631893	−15.688793	−15.622295	−15.530885	−15.459442
1.25	−15.636212	−15.693052	−15.610177	−15.508412	−15.494663
1.50	−15.637743	−15.694952	−15.597893	−15.530887	−15.488922
1.75	−15.634550	−15.692845	−15.583787	−15.565031	−15.507572
2.00	−15.624821	−15.685217	−15.594389	−15.566038	−15.525504
2.25	−15.607503	−15.671167	−15.617303	−15.543518	−15.538060
2.50	−15.582541	−15.650743	−15.633228	−15.544405	−15.516656
2.75	−15.550948	−15.642510	−15.625031	−15.544398	−15.493360
3.00	−15.569582	−15.646204	−15.596108	−15.538431	−15.510903
3.25	−15.568183	−15.645988	−15.566798	−15.543336	−15.527228
3.50	−15.564771	−15.644185	−15.574534	−15.542739	−15.511569
3.75	−15.563476	−15.642923	−15.600813	−15.561380	−15.514386
4.00	−15.564207	−15.640040	−15.616411	−15.587029	−15.508473

II. MULTIREFERENCE SYSTEMS

TABLE IV. FCI and CCSD(T) ground-state energies (in E_h) for the cationic, neutral, and anionic states of the multireference systems considered in this study. The Hartree-Fock ground-state energy (solution #1) of the neutral state is also reported.

		FCI energies			CCSD(T) energies		
System	HF energy	Cation	Neutral	Anion	Cation	Neutral	Anion
B_2	−49.0422	−48.9484	−49.2781	−49.3465	−48.9461	−49.2699	−49.3430
LiF	−106.9856	−106.8850	−107.3012	−107.3021	−106.9039	−107.3201	−107.3209
BeO	−89.4427	−89.3772	−89.7435	−89.8159	−89.3767	−89.7421	−89.8146
BN	−78.9085	−78.8315	−79.2698	−79.3797	−78.8293	−79.2697	−79.3754
C_2	−75.4036	−75.3291	−75.7866	−75.8968	−75.3274	−75.7845	−75.8945
O_3	−224.3521	−224.6858	−225.1480	−225.1951	−224.6750	−225.1419	−225.1926

TABLE V. Principal IP, principal EA, and fundamental gap (in eV) for a selection of multireference systems computed at the G_0W_0 level with different starting points (HF, BLYP, B3LYP, CAM-B3LYP) with the def2-TZVPP basis. The error with respect to the reference FCI value is reported in parentheses. See the main manuscript for more details.

		G_0W_0				
Mol.		HF(#1)	BLYP	B3LYP	CAM-B3LYP	FCI
B_2	IP	9.06(+0.09)	8.61(−0.36)	8.58(−0.39)	8.80(−0.17)	8.97
	EA	2.05(+0.19)	2.22(+0.36)	2.36(+0.50)	2.13(+0.27)	1.86
	Gap	7.01(−0.11)	6.39(−0.72)	6.23(−0.88)	6.66(−0.45)	7.11
LiF	IP	11.31(−0.01)	9.65(−1.67)	10.45(−0.87)	11.11(−0.22)	11.32
	EA	0.01(−0.01)	0.25(+0.23)	0.18(+0.16)	0.07(+0.05)	0.02
	Gap	11.29(−0.01)	9.90(−1.40)	10.62(−0.68)	11.18(−0.12)	11.30
BeO	IP	9.76(−0.21)	9.46(−0.51)	9.38(−0.59)	9.84(−0.13)	9.97
	EA	2.09(+0.12)	1.66(−0.31)	2.05(+0.08)	1.97(+0.00)	1.97
	Gap	7.67(−0.32)	7.81(+0.19)	7.34(−0.56)	7.88(−0.12)	8.00
BN	IP	11.69(−0.24)	10.79(−1.14)	11.29(−0.64)	11.57(−0.36)	11.93
	EA	3.83(+0.84)	3.82(+0.82)	3.63(+0.64)	3.53(+0.54)	2.99
	Gap	7.86(−1.08)	6.97(−1.97)	7.66(−1.28)	8.03(−0.91)	8.94
C_2	IP	12.92(+0.48)		12.22(−0.23)	12.47(+0.02)	12.45
	EA	4.08(+1.08)		3.96(+0.96)	3.88(+0.88)	3.00
	Gap	8.85(−0.60)		8.26(−1.19)	8.59(−0.86)	9.45
O_3	IP	13.50(+0.92)	11.79(−0.79)	12.26(−0.32)	12.80(+0.22)	12.58
	EA	1.96(+0.68)	1.96(+0.68)	1.96(+0.68)	1.98(+0.70)	1.28
	Gap	11.54(+0.25)	9.82(−1.47)	10.30(−0.99)	10.82(−0.47)	11.29

The G_0W_0 results computed with Kohn-Sham (KS) starting points for the multireference molecules studied in the main manuscript are reported in Table V. First of all, the stability analysis reveals that all density-functional approximations employed here lead to one stable restricted solution only. The performance of G_0W_0@KS shows that only G_0W_0@CAM-B3LYP produces competitive IPs, EAs, and gaps when compared to the G_0W_0@HF(#1) results. Notably, substantial errors of approximately 0.9 eV in gaps can still arise. It is noteworthy to mention that, for C_2, the BLYP KS determinant exhibits a non-Aufbau filling, rendering it impossible to compute the G_0W_0 correction. One way to eschew this difficulty is to rely on the Tamm–Dancoff approximation for the computation of the polarizability but we have not pursued this possibility here.

III. TRIANGULAR-SHAPED H_6 CLUSTER

- Geometry of the H_6 cluster with triangular arrangement (in Å):

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H  0.00000000000  0.00000000000  0.00000000000
H  1.00000000000  1.73205080757  0.00000000000
H  2.00000000000  0.00000000000  0.00000000000
H  3.00000000000  1.73205080757  0.00000000000
H  4.00000000000  0.00000000000  0.00000000000
H  2.00000000000  3.46410161514  0.00000000000
```

IV. DISSOCIATION CURVE OF HF

TABLE VI. IPs (in eV) of the HF molecule as a function of the internuclear distance $R_{\mathrm{H-F}}$ (in Å) computed at various levels of theory with the cc-pVDZ basis set.

$R_{\mathrm{H-F}}$	FCI	RHF	UHF	G_0W_0@RHF	G_0W_0@UHF	qsGW@RHF	qsGW@UHF
0.50	17.29	18.62	18.62	17.26	17.26	17.39	17.39
0.55	17.06	18.40	18.40	17.05	17.05	17.17	17.17
0.60	16.84	18.20	18.20	16.84	16.84	16.95	16.95
0.65	16.61	18.00	18.00	16.63	16.63	16.73	16.73
0.70	16.39	17.81	17.81	16.41	16.41	16.52	16.52
0.75	16.16	17.63	17.63	16.20	16.20	16.30	16.30
0.80	15.94	17.46	17.46	16.00	16.00	16.09	16.10
0.85	15.72	17.31	17.31	15.79	15.79	15.90	15.90
0.90	15.51	17.16	17.16	15.60	15.60	15.70	15.70
0.95	15.31	17.03	17.03	15.41	15.41	15.52	15.52
1.00	15.11	16.90	16.90	15.24	15.24	15.35	15.35
1.05	14.92	16.79	16.79	15.06	15.06	15.19	15.19
1.10	14.74	16.69	16.69	14.90	14.90	15.04	15.04
1.15	14.57	16.60	16.60	14.75	14.75	14.91	14.91
1.20	14.40	16.52	16.52	14.60	14.60	14.78	14.78
1.25	14.25	16.45	16.45	14.46	14.46	14.66	14.66
1.30	14.11	16.38	16.24	14.32	14.31	14.54	14.54
1.35	13.98	16.32	15.34	14.20	14.54	14.44	14.44
1.40	13.86	16.02	14.95	14.07	14.81	14.35	14.35
1.45	13.75	15.69	14.71	13.96	15.06	14.26	14.26
1.50	13.65	15.38	14.53	13.84	14.83	14.17	14.17
1.55	13.57	15.08	14.40	13.74	14.59	14.10	14.08
1.60	13.50	14.80	14.30	13.63	14.39	14.02	14.12
1.65	13.43	14.53	14.22	13.53	14.22	13.95	14.31
1.70	13.38	14.28	14.15	13.44	14.09	13.89	14.38
1.75	13.34	14.04	14.09	13.34	13.98	13.82	14.21
1.80	13.31	13.82	14.04	13.25	13.90	13.77	14.05
1.85	13.29	13.61	14.00	13.16	13.83	13.71	13.91
1.90	13.27	13.41	13.96	13.08	13.77	13.65	13.80
1.95	13.26	13.21	13.93	12.99	13.72	13.60	13.71
2.00	13.26	13.03	13.90	12.91	13.69	13.55	13.65
2.05	13.26	12.86	13.88	12.83	13.66	13.50	13.60
2.10	13.27	12.70	13.86	12.76	13.63	13.46	13.57
2.15	13.28	12.54	13.84	12.68	13.61	13.38	13.55
2.20	13.30	12.39	13.82	12.61	13.60	13.27	13.53
2.25	13.31	12.25	13.80	12.54	13.58	13.17	13.52
2.30	13.33	12.11	13.79	12.48	13.57	13.07	13.51
2.35	13.34	11.98	13.78	12.41	13.56	12.98	13.51
2.40	13.36	11.86	13.77	12.30	13.55	12.89	13.50
2.45	13.38	11.74	13.75	12.20	13.54	12.80	13.50
2.50	13.39	11.62	13.75	12.11	13.54	12.72	13.50
2.55	13.40	11.51	13.74	12.01	13.53	12.64	13.49
2.60	13.42	11.41	13.73	11.93	13.53	12.57	13.49
2.65	13.43	11.31	13.72	11.85	13.52	12.50	13.49
2.70	13.44	11.21	13.71	11.77	13.52	12.43	13.49
2.75	13.46	11.12	13.71	11.69	13.51	12.37	13.49
2.80	13.47	11.03	13.70	11.62	13.51	12.31	13.48
2.85	13.48	10.95	13.70	11.55	13.50	12.25	13.48
2.90	13.48	10.86	13.69	11.49	13.50	12.19	13.48
2.95	13.49	10.79	13.68	11.43	13.50	12.14	13.48
3.00	13.50	10.71	13.68	11.37	13.49	12.09	13.48
3.05	13.51	10.64	13.68	11.31	13.49	12.04	13.47
3.10	13.51	10.57	13.67	11.26	13.49	12.00	13.47
3.15	13.52	10.50	13.67	11.21	13.49	11.95	13.47
3.20	13.52	10.44	13.66	11.16	13.48	11.91	13.47
3.25	13.53	10.38	13.66	11.12	13.48	11.87	13.47
3.30	13.53	10.32	13.66	11.07	13.48	11.83	13.46
3.35	13.53	10.26	13.65	11.03	13.48	11.80	13.46
3.40	13.54	10.21	13.65	10.99	13.47	11.76	13.46
3.45	13.54	10.15	13.65	10.96	13.47	11.73	13.46
3.50	13.54	10.10	13.65	10.92	13.47	11.70	13.46

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