Article

Physi–Sorption of H_2 on Pure and Boron–Doped Graphene Monolayers: A Dispersion–Corrected DFT Study

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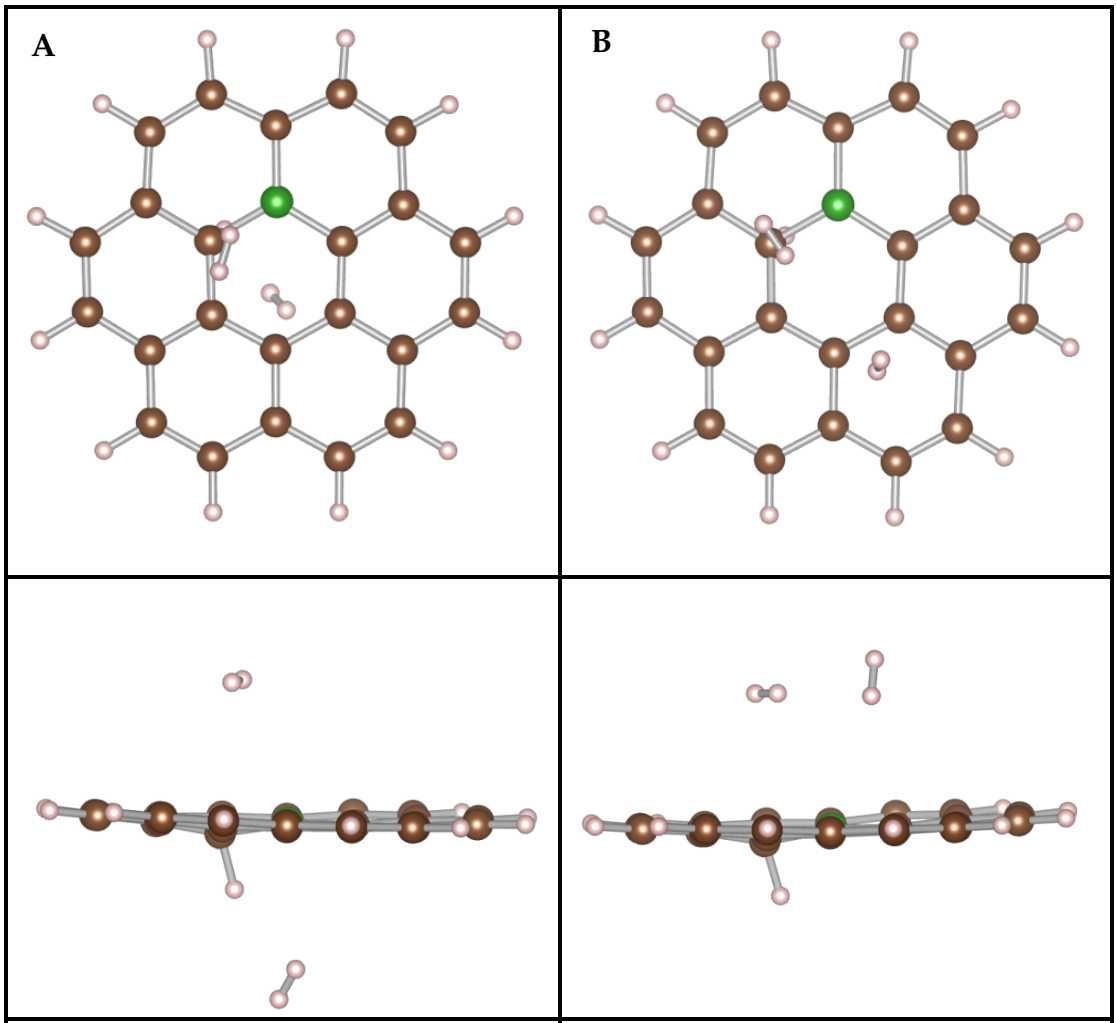


PANEL A: ΔE_b = –7.3 kJ/mol H_2	PANEL B: ΔE_b = –7.0 kJ/mol H_2

Figure S1. Free energy of binding (ΔE_b) for a second H_2 molecule on the boron–doped model. For the interaction depicted in panel A, the second H_2 molecule binds 0.3 kJ/mol weaker than the first H_2, and for the one on boron it is 0.6 kJ/mol weaker than the first H_2.

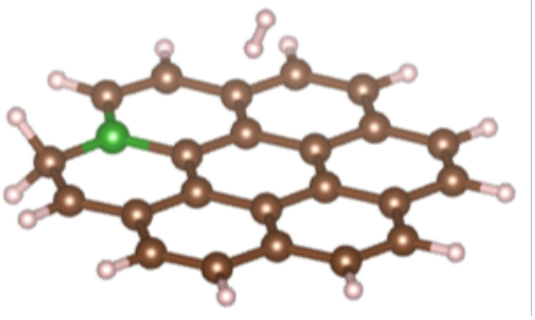
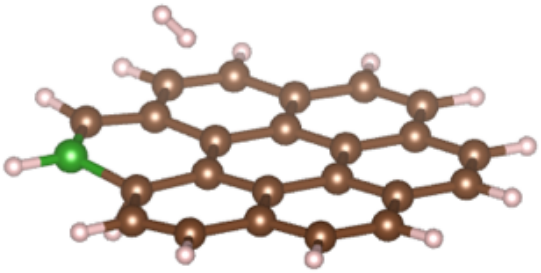
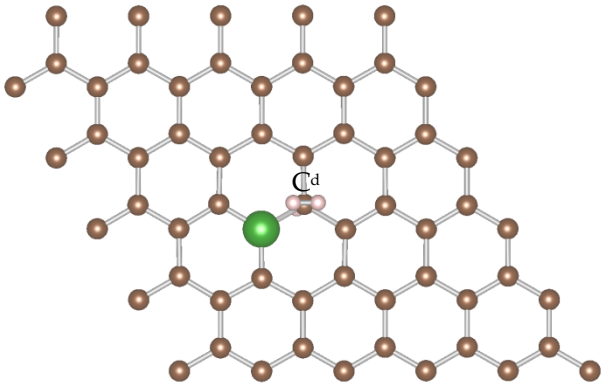
	
ΔE_b = –6.3 kJ/mol H_2	ΔE_b = –6.2 kJ/mol H_2

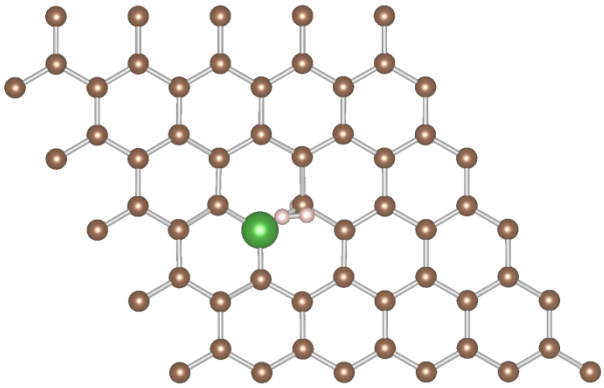
Figure S2. Molecular models and H_2 binding energies of systems where boron doping is at the edge.

Table S1. H_2 binding energy (ΔE_b in kJ/mol H_2) for different DFT exchange methods using the vdW–DF1 dispersion correction for two different monolayer spacing between the graphene sheets. In all cases the binding energy is overestimated.

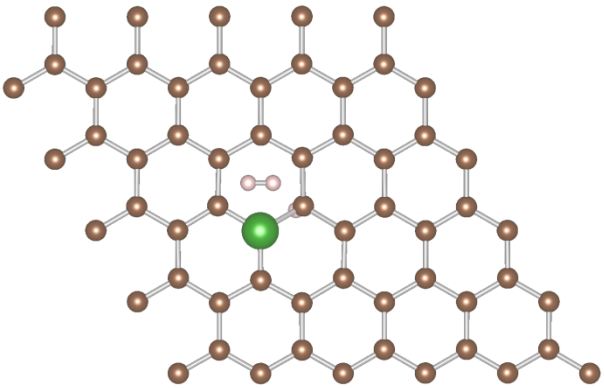
Interlayer Spacing	DFT Exchange		
	PBE	optPBE	RPBE
d = 15 Å	–9.5	–8.3	–8.8
d = 7 Å	–19.0	–16.2	−17.5



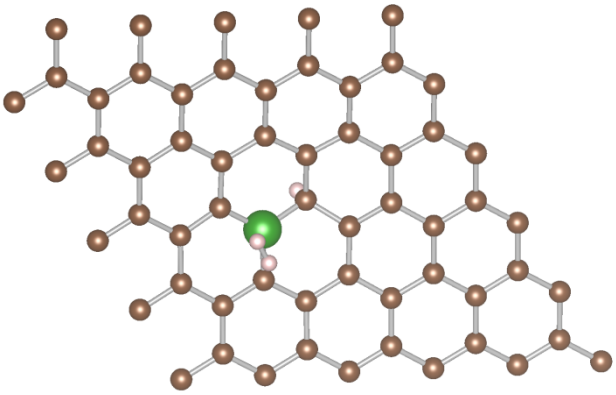
'top' Cd site (ΔE_b = –6.6 kJ/mol H_2)



'bridge' B–Cd site (ΔE_b = –6.6 kJ/mol H_2)



'hollow' site (ΔE_b = –5.8 kJ/mol H_2)



'bridge' B–C (ΔE_b = –5.3 kJ/mol H_2)

Figure S3. Different interactions sites for H_2 physi–sorption on boron–doped graphene with its calculated binding energy (ΔE_b) graphene and its 2% boron–doped variation at an interlayer distance of 15 Å. We find H_2 prefers to interact with the puckered C atom (C^d)

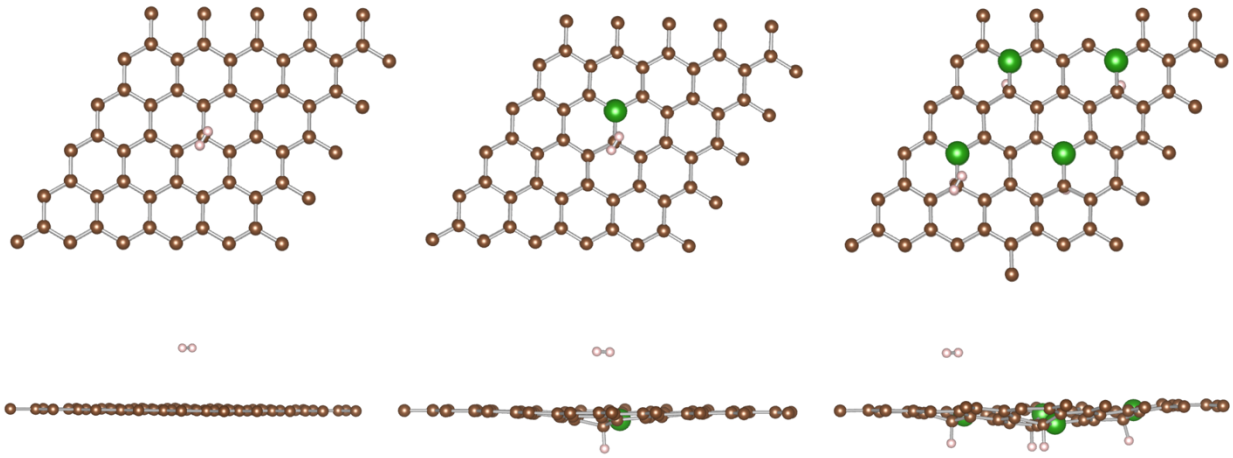


Figure S4. Top and side view of H_2 interaction at different boron–doped concentrations (0%, left; 2%, middle; and 7%, right) of graphene, reported in Figure 2 in the main text.

Distance between monolayers	d = 7Å			d = 15Å		
Level of theory	**C_{50}**	**C_{50} with H_2**	**H_2**	**C_{50}**	**C_{50} with H_2**	**H_2**
PBE	–462.15	–468.95	–6.77			
PBE–Zero damping	–462.15	–468.93	–6.77			
PBE–Becke Johnson damping	–462.15	–468.93	–6.77			
PBE–vdW–DF1	–387.28	–394.61	–7.13			
RPBE–vdW–DF1	–366.82	–374.44	–7.41	–366.64	–374.14	–7.41
optPBE–vdW–DF1	–386.95	–394.17	–7.05	–386.77	–393.91	–7.05
revPBE– vdW–DF1						
RPBE–vdW–DF2	–369.35	–377.00	–7.54	–369.25	–376.84	–7.54
revPBE– vdW–DF2				–372.18	–379.73	–7.51
optPBE– vdW–DF2				–389.37	–396.59	–7.18
C49BH system	**$C_{49}BH$**	**$C_{49}BH$ with H_2**	**H_2**	**$C_{49}BH$**	**$C_{49}BH$ with H_2**	**H_2**
RPBE–vdW–DF2	–369.66	–377.31	–7.54	–369.56	–377.16	–7.54

Table S2. Absolute electronic energies (in eV) for graphene (C50) and for boron–doped graphene (C49BH) with monolayer distances of 7Å and 15 Å.

Geometries for the molecular models with electronic energy for the model with and without H_2:

C
E (with H_2) = −923.32909
E (without H_2) = −922.14716

C	−0.38765741	3.72316232	−0.04736965
C	0.97798890	3.61311075	−0.04730415
C	1.61506311	2.34108922	−0.05127192
C	3.03037745	2.19699281	−0.04802608
C	3.61775382	0.95927554	−0.04869505
C	−1.22022481	2.56961031	−0.05156377
C	−2.64037760	2.65391313	−0.04867909
C	0.80916615	1.17308454	−0.05774002
C	−0.61171658	1.28758852	−0.05769489
C	2.83459159	−0.22840118	−0.05244598
C	1.42028938	−0.11454242	−0.05818525
C	3.41751811	−1.52615274	−0.04853989
C	−3.41835773	1.52621294	−0.04950487
C	−1.42115788	0.11446900	−0.05849426
C	−2.83548099	0.22842702	−0.05289786
C	0.61078871	−1.28749535	−0.05730618
C	1.21930290	−2.56942890	−0.05094687
C	2.63946065	−2.65378762	−0.04777482
C	−0.80993743	−1.17305143	−0.05726570
C	−3.61865683	−0.95923764	−0.04914419
C	−3.03116429	−2.19689853	−0.04823414
C	−1.61584093	−2.34095910	−0.05118016
C	0.38680212	−3.72304555	−0.04684534
C	−0.97882911	−3.61301410	−0.04693600
H	−0.85492179	4.70225793	−0.04320431
H	1.59608038	4.50471920	−0.04312714
H	3.64460983	3.09125361	−0.04400754
H	4.69893473	0.86965713	−0.04491598
H	−3.10355475	3.63496394	−0.04468968
H	−4.49993917	1.61094635	−0.04605300
H	−4.69984290	−0.86964915	−0.04571223
H	−3.64535959	−3.09118469	−0.04418991
H	0.85410343	−4.70212601	−0.04271029
H	−1.59693316	−4.50461342	−0.04288275
H	3.10259245	−3.63486275	−0.04364453
H	4.49909358	−1.61089351	−0.04481077
H	−0.00579512	−0.35707421	2.88805298
H	0.02892453	0.37702138	2.77171445

B

E (with H_2) = −910.61913
E (without H_2) =

C	−3.29780294	1.94323787	−0.03792852
C	−2.39648270	2.98399872	−0.10651462
C	−0.99027112	2.76939664	−0.16417221
C	−0.04202459	3.83289007	−0.17087197
C	1.30464542	3.58341651	−0.15141944
C	−2.84595000	0.59550563	−0.03955465
C	−3.73230720	−0.54604707	0.06077780
C	−0.51901314	1.42837990	−0.18065970
C	−1.45791594	0.37332449	−0.13464363
C	1.81896072	2.25314718	−0.13509960
C	0.90768063	1.15922093	−0.17945808
C	3.21125184	1.98607612	−0.04878877
C	−3.31998637	−1.86162550	0.08987631
C	−1.93239518	−2.21236902	0.00141475
C	1.42946236	−0.16179440	−0.16665780
C	2.80682634	−0.40650272	−0.03796642
C	3.69335755	0.70102494	0.01643767
C	0.52142265	−1.31254076	−0.29064307
C	−1.35334302	−3.48589296	0.04952288
C	0.04744089	−3.70154150	0.03890765
C	0.99904155	−2.68095486	−0.05190007
C	3.25611712	−1.77345353	0.05600650
C	2.40951001	−2.85196343	0.06952465
B	−0.97925354	−1.04814525	−0.09989628
H	−4.36052398	2.15601297	0.02451176
H	−2.75931442	4.00705708	−0.09851256
H	−0.40344668	4.85622543	−0.17028818
H	2.00834277	4.40903306	−0.13334604
H	−4.79631224	−0.33755934	0.12725708
H	−4.07612384	−2.63895980	0.18049644
H	−1.98526180	−4.36977762	0.13073573
H	0.40458003	−4.72251073	0.13378019
H	4.32419874	−1.94222096	0.15232714
H	2.81331655	−3.85115178	0.19731435
H	4.75948659	0.52238133	0.10848292
H	3.89908494	2.82443818	−0.01519830
H	0.16108266	−1.09933885	2.66992094
H	0.74569715	−0.64512187	2.58987397
H	0.17316962	−1.31237061	−1.37420181

BB ortho
E (with H_2) = −896.700915234262
E (without H_2) =

C	−2.30675190	3.11820555	0.02597970

C	−1.04645517	3.65968622	−0.00375994
C	0.21641319	2.90369645	−0.05676773
C	1.49517035	3.51734830	−0.05391470
C	2.63301460	2.73399538	−0.07789847
C	−2.48445871	1.68089417	−0.00822191
C	−3.62841829	0.91760435	0.08146232
C	0.16446481	1.50310906	−0.09724826
C	2.59251383	1.30838349	−0.10029030
C	1.32371178	0.67698800	−0.11066000
C	3.78000275	0.50869054	−0.10360825
C	−3.69768129	−0.57460803	0.08401598
C	−2.62924489	−1.44110563	−0.00112893
C	1.25521932	−0.79599495	−0.11137984
C	2.46000857	−1.54238369	−0.10031966
C	3.71655742	−0.85626728	−0.10349047
C	0.02448236	−1.51079623	−0.09925779
C	−2.58586022	−2.88875029	0.03458294
C	−1.38149565	−3.54501817	0.00148451
C	−0.05383993	−2.90983780	−0.05576213
C	2.36803850	−2.96556009	−0.07717832
C	1.16228787	−3.63969451	−0.05211530
B	−1.19538882	0.86971487	−0.11167887
B	−1.27038906	−0.75355998	−0.11002214
H	−3.16014187	3.79091033	0.08526395
H	−0.95346375	4.74178370	0.02893016
H	1.58718246	4.59866340	−0.02868714
H	3.60651752	3.21500251	−0.07271738
H	−4.60100391	1.40207384	0.18119727
H	−4.71121031	−0.96658191	0.18265921
H	−3.49792151	−3.47912947	0.09694966
H	−1.38947992	−4.63102631	0.03523461
H	3.29266228	−3.53491181	−0.07176406
H	1.15340404	−4.72483125	−0.02512687
H	4.63010911	−1.44210995	−0.10039801
H	4.74393997	1.00728086	−0.10072923
H	−1.25155236	−0.29174689	2.72597583
H	−0.95369213	0.39062165	2.69195805

BB meta $-H_2$
E (with H_2) = − 896.718027576759
E (withoutH_2) =

C	1.08447575	3.72759933	−0.16128888
C	2.35954958	3.11589908	−0.12995467
C	2.51577277	1.71965162	−0.10545518
C	3.73212875	0.96881878	−0.05579400
C	3.70760007	−0.41048056	−0.01445948

C	−0.14698921	2.99521283	−0.17490414
C	−1.44272068	3.60707569	−0.16597702
C	−0.08020995	1.59739929	−0.16696977
C	2.51114098	−1.26122747	−0.01247382
C	1.26256695	−0.64938203	−0.07087421
C	2.57562520	−2.68829249	0.05725498
C	−2.65373895	2.87689168	−0.13954817
C	−2.67640970	1.47210204	−0.11582824
C	0.06386093	−1.42671714	−0.04907260
C	0.13093962	−2.83733849	0.02745512
C	1.42403693	−3.44314436	0.07481803
C	−1.20326522	−0.76699968	−0.07571148
C	−3.81577886	0.60871270	−0.07124673
C	−3.66000940	−0.76199909	−0.03014071
C	−2.38812062	−1.49495459	−0.02286138
C	−1.09877671	−3.56355057	0.06900774
C	−2.31686631	−2.92176106	0.04627658
B	1.21237390	0.88957902	−0.12576917
B	−1.29976369	0.76978325	−0.13091243
H	1.04817097	4.81458540	−0.16747114
H	3.22925529	3.77024846	−0.11775627
H	4.69931766	1.46743339	−0.04470213
H	4.66283405	−0.92862049	0.02697752
H	−1.51003072	4.69255205	−0.17212395
H	−3.58183977	3.44543980	−0.13076017
H	−4.82616831	1.01263388	−0.06400939
H	−4.56175980	−1.36866751	0.00681467
H	−1.06451443	−4.64701461	0.12649472
H	−3.23158079	−3.50506746	0.08632614
H	1.49283823	−4.52493681	0.13267767
H	3.54154867	−3.18184745	0.10186855
H	0.15476861	−1.40959849	3.46330000
H	0.15607801	−1.40678017	2.71831938

BB−para H_2
E (with H_2) = −896.728091217039
E (without H_2) =

C	−0.78437235	3.73473778	0.01349351
C	0.59579922	3.73882662	0.06266228
C	1.34482002	2.52259976	0.05665482
C	2.76659479	2.43096106	0.10975781
C	3.49952631	1.23315976	0.10915726
C	−1.52411705	2.51423943	−0.04461334
C	−2.94532077	2.41419773	−0.09208355
C	0.60624967	1.31143107	−0.00419637

C	−0.77625569	1.30730183	−0.05213098
C	2.88724349	−0.03625893	0.05700347
C	3.50882036	−1.30165249	0.05850697
C	−3.66881726	1.21130838	−0.14263360
C	−3.04628376	−0.05458193	−0.15045295
C	0.61667774	−1.39839080	−0.05059812
C	1.36433464	−2.60585282	−0.04248526
C	2.78474541	−2.50531914	0.01134318
C	−0.76566230	−1.40238416	−0.10069133
C	−3.65865493	−1.32411902	−0.19420020
C	−2.92576477	−2.52310149	−0.19186257
C	−1.50450423	−2.61456060	−0.14570501
C	0.62439602	−3.82693888	−0.08897175
C	−0.75564441	−3.83101095	−0.13866904
B	1.35740386	−0.04115201	−0.00102210
B	−1.51650166	−0.04966312	−0.10313831
H	−1.31963828	4.67936741	0.02095602
H	1.12388306	4.68645972	0.10778809
H	3.32781256	3.36043941	0.15621423
H	4.58425833	1.31350833	0.15520650
H	−3.51430633	3.34007354	−0.08765204
H	−4.75455352	1.28476722	−0.17476087
H	−4.74378416	−1.40481883	−0.23043638
H	−3.48803661	−3.45248170	−0.22637973
H	1.15953643	−4.77170036	−0.08476910
H	−1.28406228	−4.77894524	−0.17254727
H	3.35385502	−3.43121325	0.01743158
H	4.59427803	−1.37572571	0.09916840
H	1.56307087	0.53362274	3.14402377
H	1.33047579	1.12901898	2.76201633

Bterm1

E (with H_2) = −910.64421497

E (without H_2) = −909.46222395

C	0.08452038	3.96832146	0.41665645
C	1.49833113	3.51983033	0.36943091
C	1.88030787	2.21325456	0.26548843
C	3.28809366	1.86858597	0.22214713
C	3.70802389	0.58934694	0.11529587
B	−0.99253408	2.82488348	0.33946882
C	−2.50625047	3.01704726	0.36379686
C	0.89618306	1.12178352	0.19269241
C	−0.47951161	1.38330477	0.22643001
C	2.76814707	−0.50316319	0.03893003
C	1.37652247	−0.22709598	0.07963268
C	3.20201989	−1.83572709	−0.07598775

C	−3.30956565	1.91743799	0.28260281
C	−1.41360204	0.30237716	0.14784450
C	−2.81056066	0.56423094	0.17405875
C	0.44363162	−1.30085367	0.00205710
C	0.90992895	−2.64273623	−0.11580931
C	2.29676718	−2.87773729	−0.15131538
C	−0.95495586	−1.03843024	0.03591207
C	−3.70512022	−0.52143087	0.09029376
C	−3.26126285	−1.82552785	−0.01792065
C	−1.88292036	−2.11657572	−0.04901521
C	−0.04452874	−3.70425156	−0.19620638
C	−1.38373850	−3.45178086	−0.16426469
H	−0.08461457	4.70434007	−0.38832431
H	2.28148236	4.27363463	0.41859894
H	4.00812914	2.67831623	0.27741066
H	4.76730779	0.35794829	0.08365828
H	−2.98904863	3.98918379	0.44150145
H	−4.39361724	2.02150378	0.29596779
H	−4.77153846	−0.32023853	0.11087035
H	−3.97443778	−2.64020323	−0.08176045
H	0.31970533	−4.72226800	−0.28497450
H	−2.09635072	−4.26725419	−0.22752859
H	2.65403014	−3.89837527	−0.24074212
H	4.26675839	−2.04066168	−0.10634251
H	−0.06913764	4.57697819	1.32444696
H	−0.07502968	0.23050101	−3.21914748
H	−0.14628215	0.38617452	−2.49466324

Bterm2

E (with H_2) = −910.62424

E (without H_2) = −909.44228732

C	−0.29565759	3.75022345	0.28304437
C	1.04296037	3.61982185	0.18197693
C	1.66785302	2.32253703	0.13389993
C	3.06951138	2.18718208	0.08569969
C	3.66874828	0.94567430	0.05753854
C	−1.18664795	2.58739091	0.30060203
B	−2.73342950	2.72359112	0.01807474
C	0.85840775	1.15443340	0.14619864
C	−0.56787624	1.25832202	0.18745709
C	2.89653319	−0.23485016	0.06722869
C	1.47777972	−0.12689453	0.10202654
C	3.48945078	−1.53284155	0.04074974
C	−3.47403021	1.42488749	−0.05196808
C	−1.36995002	0.10418320	0.12090964

C	−2.81712608	0.19746938	0.03307015
C	0.67426719	−1.30087370	0.09605181
C	1.29470789	−2.58312026	0.06586407
C	2.71994137	−2.65969401	0.04412836
C	−0.74437654	−1.18996220	0.09427108
C	−3.56207430	−1.03549379	−0.00697314
C	−2.95553275	−2.24933912	0.01409004
C	−1.52880935	−2.36967844	0.05473405
C	0.48095180	−3.73709129	0.04687959
C	−0.89116255	−3.62960268	0.03960449
H	−0.75395904	4.73070323	0.34956156
H	1.68001494	4.49736305	0.14676018
H	3.68026590	3.08353197	0.07479339
H	4.75012791	0.86522859	0.02576829
H	−3.21652027	3.81222405	0.03761264
H	−4.54867064	1.38385184	−0.21267120
H	−4.64315397	−0.96722912	−0.05850755
H	−3.54899294	−3.15746939	−0.01643011
H	0.95284155	−4.71347467	0.02893034
H	−1.50520019	−4.52372469	0.01483466
H	3.18502203	−3.63946733	0.02338217
H	4.57134818	−1.60853658	0.01766474
H	−1.74915424	2.59772045	1.31027200
H	−1.05868480	1.39522415	−2.50075790
H	−1.29485138	1.84253827	−3.04709431