Supplementary Materials

Study of the hydrogen absorption behavior of "number-sensitive" Mg atom: ultra-high hydrogen storage in MgH_n (n=1-20) clusters

Ben-Chao Zhu [1], Guang-Hui Liu [2], Ping-Ji Deng [1], Chun-Jing Liu [1], Yan-Hua Liao [3]*, Lu Zeng [4] *, and Jun Zhao [1] *

[1]School of Public Health, Hubei University of Medicine, Shiyan 442000, China

[2]Daye Special Steel Co.，Ltd, Huangshi 435100, P.R China

[3]School of Mathematics and Physics, Hubei Polytechnic University, Huangshi 435003, China

[4]College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

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Table S1. Cartesian coordinates for all optimized MgH_n (n=1-20) clusters.

MgH_1: Charge =0, Multiplicity =2, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.00000000	0.00000000	0.13476500
H	0.00000000	0.00000000	-1.61717800

MgH_2: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	-1.71252500
H	0.00000000	0.00000000	1.71252800

MgH_3: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.10722700	-0.00001700	0.00000100
H	1.54754700	-0.77515700	0.00000200
H	-1.80834500	0.00009700	0.00000400
H	1.54752200	0.77526800	0.00000200

MgH_4: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.35808100	-0.00085600	-0.00007100
H	0.38392300	-1.71363600	-0.00029600
H	0.40722300	1.71137100	0.00111600
H	-2.54866600	0.37939500	-0.00322900
H	-2.53944900	-0.36686000	0.00325500

MgH_5: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.307681	-0.066501	-0.000004
H	-0.729236	-1.716206	0.000030
H	2.279210	0.051555	0.000173
H	2.199997	-0.692446	-0.000110
H	-0.028995	1.577583	0.747766
H	-0.028802	1.577528	-0.747815

MgH_6: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.000239	0.000000	-0.000071
H	3.129896	0.37269	0.000244
H	-0.000398	1.713021	-0.000063
H	3.129897	-0.372691	0.000247
H	-0.000400	-1.713021	-0.000064

H	-3.128061	0.372694	0.000245
H	-3.128061	-0.372693	0.000246

MgH_7: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.916618	-0.214616	-0.056496
H	0.885796	1.373121	0.907012
H	6.066469	-0.494451	-0.240868
H	1.148997	0.726752	1.176633
H	-0.519051	-1.788640	0.457024
H	6.247561	0.214434	-0.374007
H	-1.826892	1.369301	-0.007415
H	-1.003459	1.174872	-1.240430

MgH_8: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.011039	-0.015617	-0.000273
H	0.012663	-0.011233	-1.713578
H	2.789391	-1.502382	0.373292
H	2.790676	-1.500688	-0.372025
H	0.007551	-0.019476	1.713038
H	-0.029512	3.120948	-0.370512
H	-0.030789	3.121588	0.37485
H	-2.83793	-1.510826	-0.373463
H	-2.834523	-1.510528	0.371671

MgH_9: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-1.37192	-0.177863	-0.174708
H	-0.884259	-1.926705	-0.384561
H	-0.161644	0.075296	2.094688
H	3.355822	3.980604	-0.298449
H	0.245454	-0.490277	1.822433
H	-2.424256	1.097228	0.232781
H	7.040698	-1.850179	0.015606
H	2.780413	4.437596	-0.183806
H	6.446356	-2.241312	-0.200641
H	0.064456	-0.947899	-1.001560

MgH_{10}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.001835	0.018277	0
H	-0.002403	0.025566	1.714007

H	-2.305117	2.16316	0.372656
H	-2.305096	2.163183	-0.372657
H	2.096007	-2.211896	-0.372802
H	2.324993	2.132323	0.372673
H	2.096003	-2.211899	0.372798
H	-2.102488	-2.218849	-0.372797
H	-2.10249	-2.218844	0.372783
H	2.324989	2.132339	-0.372658
H	-0.002377	0.025597	-1.714007

MgH_{11}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	1.261721	0.973041	0.139146
H	0.701410	-2.699303	-0.074631
H	0.359869	-2.105043	1.254799
H	-4.331300	3.725465	1.475292
H	-7.563002	-0.547467	-0.860410
H	-3.765866	4.006758	1.867939
H	-0.888041	0.042065	-0.868109
H	-7.411321	-0.992705	-1.436388
H	3.351673	4.847624	-1.002952
H	2.129097	0.434747	-0.267476
H	-1.176011	-0.612149	-0.647061
H	3.452844	5.576503	-1.110760

MgH_{12}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.009818	-0.000516	-0.000002
H	0.139146	3.131856	-0.372530
H	-0.074631	3.131799	0.372729
H	1.254799	-2.381898	0.372680
H	1.475292	1.184752	0.372624
H	-0.860410	0.750929	0.372483
H	1.867939	0.750923	-0.372668
H	-0.868109	1.184737	-0.372737
H	-1.436388	-2.682071	-0.372552
H	-1.002952	-2.682042	0.372660
H	-0.267476	-0.000439	-1.714456
H	-0.647061	-2.381906	-0.372660
H	-1.110760	-0.000446	1.714453

MgH_{13}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z

Mg	0.424306	-0.150039	-0.249728
H	0.186754	3.706821	3.620501
H	0.549371	-2.189191	-1.829874
H	-0.195414	-2.121651	-1.807412
H	-1.267734	-0.536908	0.322655
H	-5.768980	2.946357	-2.766643
H	0.922918	3.657623	3.526850
H	-4.607116	-3.462092	3.236757
H	-1.216350	0.381628	-0.854473
H	2.123560	-0.114287	-0.148112
H	7.177956	-0.050847	-0.342902
H	-5.179851	2.575524	-2.505005
H	-4.253157	-2.949073	2.831067
H	6.436373	-0.043431	-0.286673

MgH_{14}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.451309	-0.005033	-0.071942
H	0.548805	-2.846436	-1.374904
H	-1.226521	0.004643	0.280846
H	-0.181156	-2.844248	-1.224109
H	0.194911	0.330283	-3.159559
H	0.705508	3.06529	-0.764368
H	2.130685	-0.012357	-0.416296
H	-0.024286	3.070599	-0.613338
H	-0.535322	0.334099	-3.009932
H	0.558239	-2.112643	2.311987
H	1.387662	1.573204	2.555563
H	1.287562	-2.114371	2.158988
H	0.658431	1.577976	2.708603
H	-5.831085	0.017309	0.731271
H	-5.089136	0.017048	0.678554

MgH_{15}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.618196	0.009328	-0.088668
H	-2.215248	4.471749	2.640196
H	0.052394	-1.934521	-1.651486
H	0.724607	-1.610910	-1.595119
H	0.765729	1.079814	-0.616968
H	5.740018	0.897623	3.525660
H	-2.854643	4.092424	2.619851
H	4.019754	-5.696151	-0.020941

H	3.036629	4.265419	-4.207941
H	1.070580	0.230870	0.573973
H	-2.227197	-0.547398	-0.073205
H	-6.82318	-2.656488	0.059357
H	5.134193	0.814675	3.102411
H	2.812702	3.890048	-3.606267
H	4.342804	-5.090679	0.265549
H	-6.160794	-2.318407	0.048945

MgH_{16}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.2691160	-0.633678	0.157481
H	1.9828020	-2.752838	-0.795179
H	-3.279670	-0.471320	0.920267
H	-4.793070	5.2081950	-1.033721
H	-3.333374	-0.100669	0.275752
H	-4.277937	4.9396750	-1.498017
H	-1.753657	-2.927794	-1.476222
H	1.934936	-2.384049	-1.440778
H	-0.378877	0.212189	-1.329806
H	7.719314	2.381830	-0.352457
H	-0.151285	-1.488176	1.639152
H	2.589978	0.450862	0.998201
H	7.491517	2.995377	-0.705527
H	-1.704859	-3.298451	-0.831592
H	-0.656653	1.826929	2.017846
H	-0.706070	2.191800	1.369685
H	2.546300	0.820580	0.352630

MgH_{17}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.166296	-0.432046	0.432046
H	0.442218	-5.420898	-5.420898
H	-0.522455	1.758792	1.758792
H	0.224857	1.739864	1.739864
H	1.463157	-0.771211	-0.771211
H	6.155743	1.241572	1.241572
H	-0.296533	-5.338601	-5.338601
H	1.734039	6.521918	6.521918
H	4.870929	-2.305341	-2.305341
H	1.530359	0.004386	0.004386
H	-1.849755	-0.601104	-0.601104
H	-6.753157	-1.680698	-1.680698

H	5.592304	1.021646	1.021646
H	4.505281	-2.127732	-2.127732
H	2.264952	6.04275	6.04275
H	-6.029806	-1.542599	-1.542599
H	-5.743731	3.660309	3.660309
H	-5.592846	2.981502	2.981502

MgH_{18}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.008821	-0.901872	-0.000966
H	-2.144166	4.267395	3.120445
H	-4.627300	3.589189	-1.803425
H	1.126595	1.251002	-1.908472
H	-4.900703	3.982891	-2.372029
H	-1.119232	-1.472958	-2.902868
H	-1.336806	-0.004706	0.568517
H	0.627901	-2.422744	2.752438
H	-2.011652	4.932475	3.425723
H	1.345565	-1.814202	-0.566649
H	-2.060502	-3.413154	0.230545
H	-1.476988	-3.805077	-0.016231
H	-1.70417	-1.080022	-2.660298
H	6.944535	3.094971	-1.179336
H	2.195083	0.669389	1.530741
H	1.611148	1.063027	1.775284
H	0.045085	-2.030422	3.000683
H	0.542135	1.642398	-1.661443
H	6.837617	2.373017	-1.322038

MgH_{19}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	0.381415	-0.511772	0.280508
H	-1.012696	1.664047	0.933782
H	-0.411017	4.61373	-2.317474
H	-4.965546	2.254836	-1.636239
H	0.923098	-1.132460	1.7703660
H	0.434716	0.490852	-1.247156
H	2.653009	3.972960	2.139269
H	-4.456659	-0.835148	2.534690
H	-2.597722	-4.593108	-0.682238
H	-4.327503	-1.118163	1.859254
H	2.810874	3.435318	2.628238
H	-0.803068	1.457949	1.620970

H	5.762797	-1.016904	-0.818603
H	-0.745365	-0.303031	-1.142700
H	1.671682	-2.501891	-0.971333
H	-0.347747	5.333760	-2.142514
H	6.093785	-1.389897	-1.370269
H	1.594535	-2.037317	-1.551656
H	-2.478902	-4.008458	-1.126272
H	-4.375253	1.8541930	-1.846216

MgH_{20}: Charge =0, Multiplicity =1, b3pw91/6-311+g(d)			
Atom	X	Y	Z
Mg	-0.74248	0.046462	-0.233081
H	2.264489	-0.714941	-0.120017
H	-0.173987	1.391395	-1.13154
H	-3.466897	-0.360272	-1.884114
H	5.321264	2.282437	0.922460
H	0.856294	6.174091	-0.174467
H	-2.821568	2.141954	0.904384
H	5.265501	2.085387	1.637340
H	0.746847	5.509887	-0.490747
H	-2.579906	-4.236940	2.594193
H	-3.21615	0.225400	-2.270535
H	0.004920	-1.553432	-2.877570
H	0.568346	1.554071	2.150523
H	-1.321749	-1.299775	0.656642
H	5.812074	-4.174911	-0.558938
H	0.307178	0.975957	2.541990
H	-3.068663	1.551506	1.286125
H	2.003196	-1.299864	0.261115
H	-0.245615	-2.139140	-2.490906
H	-2.827094	-4.823019	2.979842
H	5.481283	-3.847335	-1.138807

The structural optimization calculation level is B3PW91/6-311G(d) [S1, S2] for this work is based on the previous similar research on Mg-based clusters and Mg-H clusters [S3-S7]. It is worthy to note that during optimization using Gaussian09, many isomers do not converge and always reported ‘‘Gaussian l999 error’’, Due to the presence of a large number of H atoms in this cluster system, which interact weakly with Mg, we use the GIIDS method in structural optimization calculations where convergence is not possible

Reference

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[S7] Liu, Ting, et al. "Investigating the structural and electronic properties of anionic calcium-doped magnesium clusters." Journal of Molecular Structure (2023): 135195.

Table S2. E_{gap} for β-electrons, HOMO and LUMO energy of Molecular Orbitals (MOs) for all optimized MgH_n (n=1-20) clusters.

Cluster	E_{gap}-β(eV)	HOMO-α (eV)	LUMO-α (eV)	HOMO-β (eV)	LUMO-β (eV)
MgH_1	4.89	—	1.44	1.44	3.68
MgH_2	6.48	2.59	2.22	2.22	6.48
MgH_3	5.20	-3.77	1.61	1.61	4.74
MgH_4	6.23	3.75	2.25	2.25	6.23
MgH_5	5.11	-3.74	1.88	1.88	4.98
MgH_6	6.34	3.73	2.26	2.26	6.34
MgH_7	5.04	-3.72	2.00	2.00	5.50
MgH_8	6.62	3.72	2.27	2.27	6.62
MgH_9	5.05	-3.71	2.06	2.06	5.49
MgH_{10}	6.89	3.71	2.27	2.27	6.89
MgH_{11}	5.04	-3.70	2.10	2.10	5.51
MgH_{12}	6.90	3.70	2.27	2.27	6.90
MgH_{13}	5.04	-3.70	2.13	2.13	5.51
MgH_{14}	7.06	3.70	2.27	2.27	7.06
MgH_{15}	4.83	-3.70	2.15	2.15	5.77
MgH_{16}	7.07	3.70	2.27	2.27	7.07
MgH_{17}	5.05	-3.70	2.17	2.17	5.50
MgH_{18}	7.07	3.70	2.27	2.27	7.07
MgH_{19}	4.99	-3.70	2.18	2.18	5.56
MgH_{20}	7.07	—	2.28	2.28	7.07

Table S3. The atom distance in three kinds Mg-H interaction for all optimized MgH_n (n=1-20) clusters.

Clusters	Mg-H attraction distance / Å			Mg-H VdW distance / Å					Mg-H no interaction distance / Å					
	Mg-H	Mg-H	Mg-H	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2	Mg-H_2
MgH_1	1.75200	—	—	—	—	—	—	—	—	—	—	—	—	—
MgH_2	1.71300	1.71300	—	—	—	—	—	—	—	—	—	—	—	—
MgH_3	1.70161	1.82721	1.82722	—	—	—	—	—	—	—	—	—	—	—
MgH_4	1.71288	1.71288	—	2.98836	—	—	—	—	—	—	—	—	—	—
MgH_5	1.70271	1.82748	1.82756	2.59147	—	—	—	—	—	—	—	—	—	—
MgH_6	1.71379	1.71379	—	2.93379	2.93472	—	—	—	—	—	—	—	—	—
MgH_7	1.70288	1.82725	1.82726	2.68058	2.68062	—	—	—	—	—	—	—	—	—
MgH_8	1.71412	1.71412	—	3.08689	2.90616	3.07781	—	—	—	—	—	—	—	—
MgH_9	1.70296	1.82712	1.82717	2.67980	2.67961	—	—	—	5.88564	—	—	—	—	—
MgH_{10}	1.71402	1.71402	—	3.12919	3.12791	3.12633	3.12791	—	—	—	—	—	—	—
MgH_{11}	1.70306	1.82711	1.82710	2.67902	2.67870	—	—	—	5.98117	6.08208	—	—	—	—
MgH_{12}	1.71446	1.71446	—	3.14771	3.14788	3.16413	3.18103	3.16759	—	—	—	—	—	—
MgH_{13}	1.70310	1.82707	1.82710	2.67980	2.67658	—	—	—	6.08165	5.98284	6.85342	—	—	—
MgH_{14}	1.71455	1.71434	—	3.13756	3.17317	3.18912	3.15776	3.12863	5.60381	—	—	—	—	—
MgH_{15}	1.70303	1.82721	1.82712	2.67608	2.68018	—	—	—	6.81136	5.98576	6.07710	6.49964	—	—
MgH_{16}	1.71447	1.71446	—	3.15311	3.16890	3.16386	3.14375	3.13462	5.92275	5.75245	—	—	—	—
MgH_{17}	1.70298	1.82729	1.82724	2.67990	2.67529	—	—	—	6.84211	5.98054	6.08239	6.49866	6.74343	—
MgH_{18}	1.71441	1.71450	—	3.14032	3.13280	3.14963	3.16300	3.15543	5.59401	5.49598	6.88750	—	—	—
MgH_{19}	1.70298	1.82731	1.82734	2.67816	2.67816	—	—	—	5.68970	5.67690	6.87156	6.76933	6.63894	6.79833
MgH_{20}	1.71385	1.71492	—	3.14956	3.14468	3.14686	3.15397	3.15776	5.55084	6.04109	6.07328	6.69734	—	—

Table S4. ADCH analysis on Mg and H atoms in all optimized MgH_n (n=1-20) clusters.

Clusters	Mg	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11	H-12	H-13	H-14	H-15	H-16	H-17	H-18	H-19	H-20	H-21
MgH_1	0.16	-0.16																			
MgH_2	0.49	-0.25	-0.25																		
MgH_3	0.44	-0.24	-0.10	-0.10																	
MgH_4	0.57	-0.27	-0.27	-0.02	-0.02																
MgH_5	0.42	-0.12	-0.13	-0.06	-0.07	-0.03															
MgH_6	0.56	-0.02	-0.25	-0.02	-0.25	-0.02	-0.02														
MgH_7	0.34	-0.10	0.03	0.03	-0.24	0.02	-0.10	0.02													
MgH_8	0.59	-0.25	-0.02	-0.02	-0.25	-0.01	-0.01	-0.01	-0.01												
MgH_9	0.34	-0.10	0.03	0.03	-0.24	0.02	-0.10	0.02	0.00	0.00											
MgH_{10}	0.41	-0.25	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-0.25										
MgH_{11}	0.34	0.02	0.03	0.02	-0.10	0.03	-0.10	-0.24	0.00	0.00	0.00	0.00									
MgH_{12}	0.40	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-0.25	0.01	-0.25								
MgH_{13}	0.34	0.02	0.03	0.02	-0.10	0.03	-0.10	-0.24	0.00	0.00	0.00	0.00	0.00	0.00							
MgH_{14}	0.40	0.01	-0.25	0.01	0.01	0.01	-0.25	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00						
MgH_{15}	0.34	0.02	0.03	0.02	-0.10	0.03	0.00	-0.10	-0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
MgH_{16}	0.40	0.01	0.01	0.00	0.01	0.00	0.01	0.01	-0.25	0.00	-0.25	0.01	0.00	0.01	0.01	0.01	0.01				
MgH_{17}	0.34	0.02	0.03	0.02	-0.10	0.00	0.03	0.00	-0.10	-0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
MgH_{18}	0.40	0.00	0.01	0.01	-0.25	0.01	0.00	-0.25	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00		
MgH_{19}	0.34	-0.24	0.03	0.02	-0.10	0.03	0.02	0.00	0.00	0.00	0.00	-0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
MgH_{20}	0.40	0.01	0.01	0.00	0.01	0.00	0.01	0.01	-0.25	0.00	-0.25	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00

The ADCH (atomic dipole moment corrected Hirshfeld population) charge proposed by Lu Tian et al. [S8] is an improved version of Hirshfeld charge, it resolved many inherent drawbacks of Hirshfeld charge, such as poor dipole moment reproducibility. ADCH calculation can be easily obtained through Multiwfn software [S9]. For all clusters, we use a standard color rendering, i.e. an ADCH of 0.59 for the Mg atom in the MgH_8 isomer is assigned as the blue maximum, while the minimum ADCH of -0.25 for the H atom in all isomers is rendered as the red maximum. All the remaining colors are rendered accordingly to varying degrees within this range [S10].

Reference

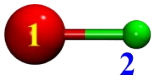
[S8] Lu, Tian, and Feiwu Chen. "Atomic dipole moment corrected Hirshfeld population method." Journal of Theoretical and Computational Chemistry 11.01 (2012): 163-183.

[S9] Tian Lu, FeiwuChen. "Multiwfn: A Multifunctional Wavefunction Analyzer." J. Comput., and Chem 33 (2012).

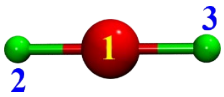
[S10] Specific ADCH plot operations can be found in section 4.7.2 of the Multiwfn manual, which can be download directly online in the following website, http://sobereva.com/multiwfn/misc/Multiwfn_3.8_dev.pdf.

Table S5. Topological analysis for all optimized MgH_n (n=1-20) clusters, including connecting atoms and numbering of bond critical points (BCPs) bonding, electron density, Laplacian of electron density, ELF and atom distance.

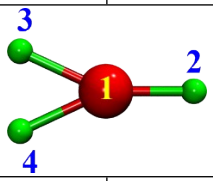
Table S5-1. MgH_n (n=1,2,3,4)



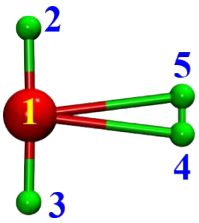
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_1	1(Mg)--2(H)	0.04733	0.16932	0.13200	1.75194



Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_2	1(Mg)--2(H)	0.05206	0.19550	0.13359	1.71253
	3(H)--1(Mg)	0.05206	0.19550	0.13359	1.71253

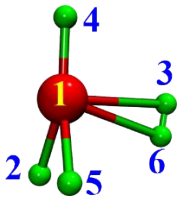


Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_3	3(H)--1(Mg)	0.03923	0.13416	0.11518	1.82721
	2(H)--1(Mg)	0.05292	0.20079	0.13405	1.70161
	3(H)--4(H)	0.05056	0.03535	0.58727	1.55027
	1(Mg)--4(H)	0.03923	0.13416	0.11518	1.82722

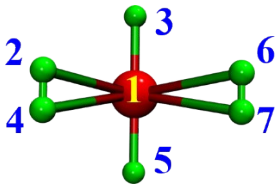


Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_4	3(H)--1(Mg)	0.05197	0.19573	0.13308	1.71288
	4(H)--1(Mg)	0.00377	0.00794	0.02524	2.98836
	4(H)--5(H)	0.24357	-0.87491	1.00000	0.74604
	1(Mg)--5(H)	0.00377	0.00794	0.02524	2.98843
	1(Mg)--2(H)	0.05197	0.19573	0.13308	1.71288

Table S5-2. MgH_n (n=5,6)

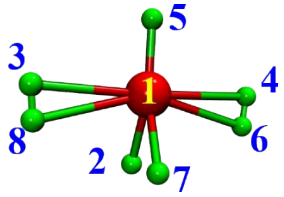


Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_5	4(H)--1(Mg)	0.05271	0.20063	0.13328	1.70271
	3(H)--6(H)	0.24215	-0.86471	1.00000	0.74816
	1(Mg)--3(H)	0.00666	0.02394	0.01759	2.58656
	1(Mg)--6(H)	0.00664	0.01732	0.02816	2.59147
	1(Mg)--6(H)	0.00666	0.02394	0.01759	2.59147
	1(Mg)--2(H)	0.03916	0.13705	0.11159	1.82756
	1(Mg)--5(H)	0.03916	0.13709	0.11158	1.82748
	2(H)--5(H)	0.05446	0.03590	0.60341	1.49548

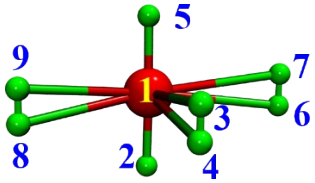


Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_6	6(H)--7(H)	0.24342	-0.87386	1.00000	0.74626
	6(H)--1(Mg)	0.00410	0.00847	0.02805	2.93472
	7(H)--1(Mg)	0.00409	0.00847	0.02797	2.9352
	3(H)--1(Mg)	0.05182	0.19573	0.13241	1.71379
	1(Mg)--5(H)	0.05182	0.19573	0.13242	1.71379
	1(Mg)--2(H)	0.00410	0.00848	0.02808	2.93379
	1(Mg)--4(H)	0.00410	0.00848	0.02808	2.9338
	2(H)--4(H)	0.24342	-0.87385	1.00000	0.74626

Table S5-3. MgH_n (n=7,8)

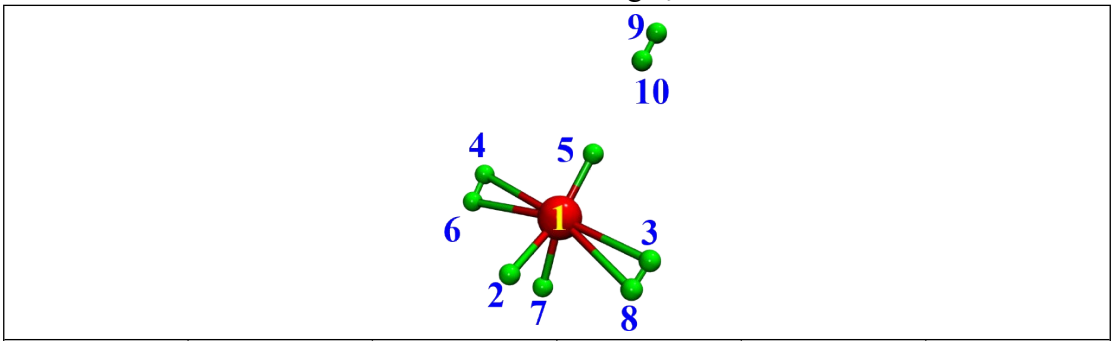


Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_7	2(H)--7(H)	0.05919	0.03348	0.62703	1.43815
	2(H)--1(Mg)	0.03919	0.14037	0.10839	1.82725
	7(H)--1(Mg)	0.03919	0.14036	0.10839	1.82726
	8(H)--1(Mg)	0.00595	0.01442	0.02897	2.68058
	8(H)--3(H)	0.24266	-0.86833	1.00000	0.74738
	6(H)--1(Mg)	0.00595	0.01442	0.02896	2.68062
	6(H)--4(H)	0.24266	-0.86833	1.00000	0.74738
	1(Mg)--5(H)	0.05268	0.20081	0.13305	1.70288



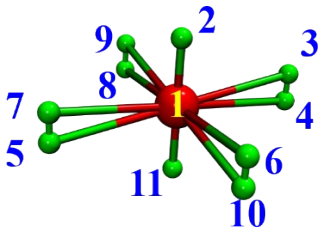
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_8	5(H)--1(Mg)	0.05176	0.19587	0.13209	1.71412
	1(Mg)--7(H)	0.00324	0.00710	0.02050	3.08689
	7(H)--6(H)	0.24386	-0.87688	1.00000	0.74559
	1(Mg)--6(H)	0.00324	0.00710	0.02050	3.08689
	1(Mg)--2(H)	0.05176	0.19587	0.13209	1.71412
	1(Mg)--9(H)	0.00329	0.00718	0.02091	3.07781
	1(Mg)--8(H)	0.00329	0.00718	0.02091	3.07785
	9(H)--8(H)	0.24384	-0.87672	1.00000	0.74562
	1(Mg)--3(H)	0.00428	0.00876	0.02970	2.90616
	1(Mg)--4(H)	0.00428	0.00876	0.02970	2.90614
	3(H)--4(H)	0.24335	-0.87329	1.00000	0.74639

Table S5-4. MgH_9



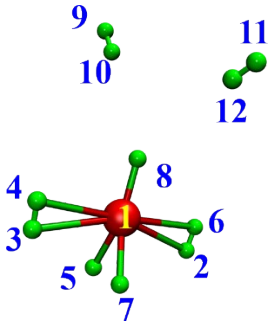
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_9	8(H)--3(H)	0.24265	-0.86830	1.00000	0.74739
	8(H)--1(Mg)	0.00596	0.01443	0.02902	2.67961
	7(H)--2(H)	0.05912	0.03353	0.62673	1.43896
	7(H)--1(Mg)	0.03920	0.14038	0.10845	1.82712
	2(H)--1(Mg)	0.03920	0.14035	0.10846	1.82717
	1(Mg)--5(H)	0.05266	0.20086	0.13292	1.70296
	10(H)--9(H)	0.24496	-0.88388	1.00000	0.74377
	1(Mg)--6(H)	0.00596	0.01443	0.02901	2.6798

Table S5-5. MgH_{10}



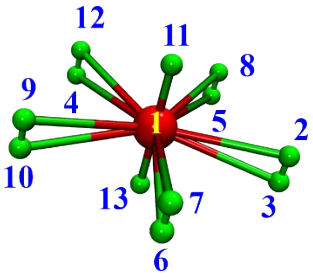
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{10}	10(H)--1(Mg)	0.00303	0.00673	0.01878	3.12919
	11(H)--1(Mg)	0.05179	0.19612	0.13205	1.71402
	10(H)--6(H)	0.24395	-0.87748	1.00000	0.74545
	5(H)--1(Mg)	0.00304	0.00674	0.01883	3.12791
	5(H)--7(H)	0.24395	-0.87747	1.00000	0.74545
	1(Mg)--4(H)	0.00304	0.00674	0.01883	3.12791
	1(Mg)--8(H)	0.00304	0.00676	0.01890	3.12633
	6(H)--1(Mg)	0.00303	0.00673	0.01878	3.12919
	7(H)--1(Mg)	0.00304	0.00674	0.01883	3.12791
	4(H)--3(H)	0.24395	-0.87747	1.00000	0.74545
	1(Mg)--3(H)	0.00304	0.00674	0.01883	3.12791
	8(H)--9(H)	0.24395	-0.87745	1.00000	0.74546
	1(Mg)--2(H)	0.05179	0.19612	0.13205	1.71402
	1(Mg)--9(H)	0.00304	0.00676	0.01890	3.12633

Table S5-6. MgH_{11}



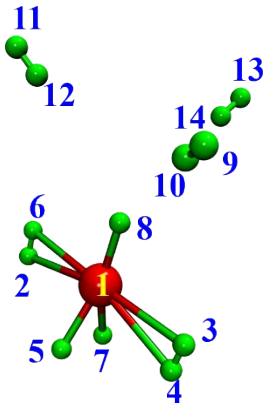
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{11}	11(H)--12(H)	0.24499	-0.88406	1.00000	0.74739
	2(H)--6(H)	0.24265	-0.86827	1.00000	0.74739
	2(H)--1(Mg)	0.00597	0.01445	0.02905	2.6787
	7(H)--1(Mg)	0.03920	0.14038	0.10846	1.8271
	7(H)--5(H)	0.05912	0.03353	0.62673	1.43904
	1(Mg)--5(H)	0.03920	0.14038	0.10846	1.82711
	1(Mg)--8(H)	0.05264	0.20078	0.13292	1.70306
	1(Mg)--4(H)	0.00597	0.01444	0.02905	2.67902
	4(H)--3(H)	0.24265	-0.86829	1.00000	0.74739
	10(H)--9(H)	0.24498	-0.88404	1.00000	0.74372

Table S5-7. MgH_{12}



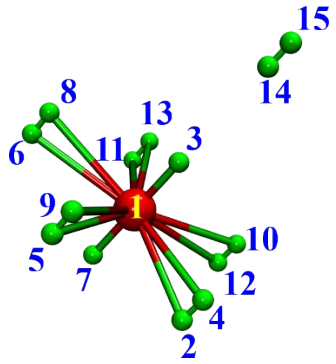
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{12}	9(H)--10(H)	0.24410	-0.87845	1.00000	0.74525
	7(H)--6(H)	0.24406	-0.87818	1.00000	0.74531
	9(H)--1(Mg)	0.00285	0.00638	0.01743	3.16759
	10(H)--1(Mg)	0.00285	0.00638	0.01743	3.16759
	7(H)--1(Mg)	0.00295	0.00654	0.01822	3.14771
	6(H)--1(Mg)	0.00295	0.00654	0.01822	3.14771
	11(H)--1(Mg)	0.05171	0.19622	0.13161	1.71446
	1(Mg)--12(H)	0.00279	0.00627	0.01691	3.18103
	12(H)--4(H)	0.24413	-0.87863	1.00000	0.74521
	1(Mg)--4(H)	0.00279	0.00627	0.01691	3.18104
	1(Mg)--13(H)	0.05171	0.19622	0.13161	1.71446
	1(Mg)--2(H)	0.00295	0.00654	0.01821	3.14788
	1(Mg)--3(H)	0.00295	0.00654	0.01821	3.14788
	1(Mg)--8(H)	0.00287	0.00641	0.01756	3.16413
	1(Mg)--5(H)	0.00287	0.00641	0.01757	3.16411
	2(H)--3(H)	0.24406	-0.87818	1.00000	0.74531
	8(H)--5(H)	0.24410	-0.87840	1.00000	0.74526

Table S5-8. MgH_{13}



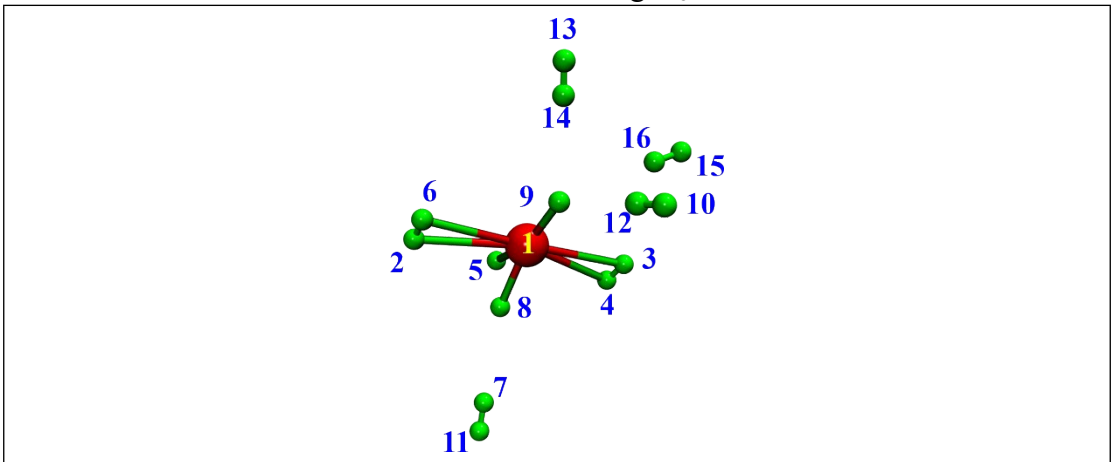
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{13}	4(H)--3(H)	0.24264	-0.86824	1.00000	0.7474
	13(H)--14(H)	0.24501	-0.88420	1.00000	0.74367
	4(H)--1(Mg)	0.00599	0.01449	0.02920	2.67658
	5(H)--7(H)	0.05914	0.03351	0.62683	1.43884
	5(H)--1(Mg)	0.03920	0.14039	0.10845	1.8271
	7(H)--1(Mg)	0.03921	0.14041	0.10845	1.82707
	1(Mg)--8(H)	0.05264	0.20077	0.13290	1.7031
	9(H)--10(H)	0.24499	-0.88405	1.00000	0.74372
	1(Mg)--2(H)	0.00596	0.01443	0.02903	2.6798
	2(H)--6(H)	0.24265	-0.86830	1.00000	0.74738
	12(H)--11(H)	0.24499	-0.88407	1.00000	0.74372

Table S5-9. MgH_{14}



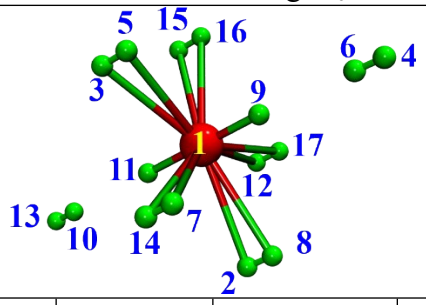
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{14}	4(H)--2(H)	0.24404	-0.87802	1.00000	0.74535
	10(H)--12(H)	0.24411	-0.87853	1.00000	0.74523
	4(H)--1(Mg)	0.00299	0.00662	0.01862	3.13756
	2(H)--1(Mg)	0.00301	0.00664	0.01875	3.13595
	10(H)--1(Mg)	0.00283	0.00633	0.01722	3.17317
	12(H)--1(Mg)	0.00283	0.00634	0.01728	3.17203
	15(H)--14(H)	0.24493	-0.88370	1.00000	0.74382
	3(H)--1(Mg)	0.05168	0.19629	0.13143	1.71455
	1(Mg)--7(H)	0.05173	0.19627	0.13165	1.71434
	1(Mg)--9(H)	0.00304	0.00670	0.01902	3.12863
	1(Mg)--5(H)	0.00304	0.00671	0.01907	3.12774
	9(H)--5(H)	0.24402	-0.87789	1.00000	0.74538
	1(Mg)--13(H)	0.00275	0.00620	0.01660	3.18912
	1(Mg)--11(H)	0.00276	0.00622	0.01671	3.18741
	1(Mg)--8(H)	0.00290	0.00646	0.01782	3.15776
	13(H)--11(H)	0.24414	-0.87874	1.00000	0.74518
	1(Mg)--6(H)	0.00291	0.00647	0.01789	3.15659
	8(H)--6(H)	0.24408	-0.87831	1.00000	0.74528

Table S5-10. MgH_{15}



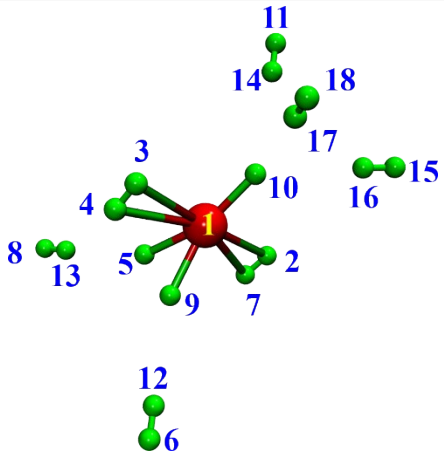
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{15}	13(H)--14(H)	0.24499	-0.88406	1.00000	0.74372
	6(H)--2(H)	0.24265	-0.86831	1.00000	0.74738
	2(H)--1(Mg)	0.00596	0.01442	0.02902	2.68018
	9(H)--1(Mg)	0.05265	0.20080	0.13293	1.70303
	12(H)--10(H)	0.24499	-0.88405	1.00000	0.74372
	1(Mg)--8(H)	0.03920	0.14046	0.10837	1.82712
	1(Mg)--5(H)	0.03920	0.14042	0.10836	1.82721
	8(H)--5(H)	0.05927	0.03342	0.62744	1.70303
	1(Mg)--4(H)	0.00599	0.01450	0.02920	2.67608
	11(H)--7(H)	0.24501	-0.88423	1.00000	0.74367
	3(H)--4(H)	0.24264	-0.86819	1.00000	0.74741
	16(H)--15(H)	0.24501	-0.88420	1.00000	0.74367

Table S5-11. MgH_{16}



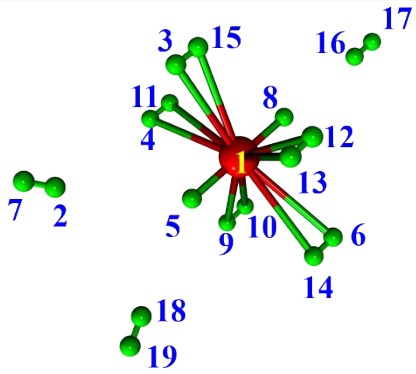
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{16}	14(H)--7(H)	0.24403	-0.87799	1.00000	0.74535
	3(H)--5(H)	0.24405	-0.87812	1.00000	0.74532
	14(H)--1(Mg)	0.00301	0.00665	0.01878	3.13462
	7(H)--1(Mg)	0.00301	0.00666	0.01881	3.13434
	3(H)--1(Mg)	0.00297	0.00657	0.01841	3.14375
	5(H)--1(Mg)	0.00297	0.00657	0.01840	3.14382
	13(H)--10(H)	0.24496	-0.88387	1.00000	0.74377
	11(H)--1(Mg)	0.05170	0.19628	0.13152	1.71447
	2(H)--1(Mg)	0.00292	0.00650	0.01804	3.15311
	2(H)--8(H)	0.24407	-0.87826	1.00000	0.74529
	8(H)--1(Mg)	0.00292	0.00649	0.01798	3.15392
	1(Mg)--9(H)	0.05170	0.19631	0.13148	1.71446
	6(H)--4(H)	0.24495	-0.88379	1.00000	0.74379
	1(Mg)--15(H)	0.00287	0.00641	0.01759	3.16386
	1(Mg)--16(H)	0.00287	0.00641	0.01762	3.16346
	1(Mg)--12(H)	0.00285	0.00637	0.01740	3.1689
	1(Mg)--17(H)	0.00284	0.00636	0.01737	3.16936
	15(H)--16(H)	0.24409	-0.87840	1.00000	0.74526
	12(H)--17(H)	0.24411	-0.87848	1.00000	0.74524

Table S5-12. MgH_{17}



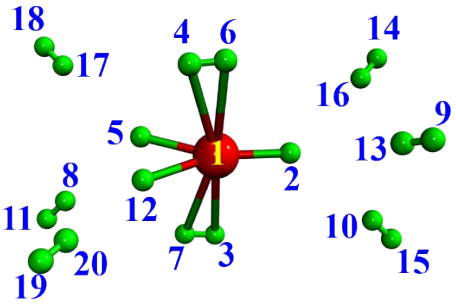
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{17}	6(H)--12(H)	0.24501	-0.88424	1.00000	0.74367
	15(H)--16(H)	0.24499	-0.88407	1.00000	0.74372
	17(H)--18(H)	0.24501	-0.88420	1.00000	0.74367
	9(H)--1(Mg)	0.03919	0.14045	0.10831	1.82724
	9(H)--5(H)	0.05932	0.03340	0.62762	1.43669
	2(H)--7(H)	0.24265	-0.86829	1.00000	0.74739
	2(H)--1(Mg)	0.00596	0.01443	0.02901	2.6799
	1(Mg)--4(H)	0.00600	0.01452	0.02923	2.67529
	1(Mg)--5(H)	0.03919	0.14042	0.10831	1.82729
	4(H)--3(H)	0.24264	-0.86818	1.00000	0.74741
	1(Mg)--10(H)	0.05265	0.20082	0.13295	1.70298
	13(H)--8(H)	0.24501	-0.88423	1.00000	0.74367
	14(H)--11(H)	0.24499	-0.88405	1.00000	0.74372

Table S5-13. MgH_{18}



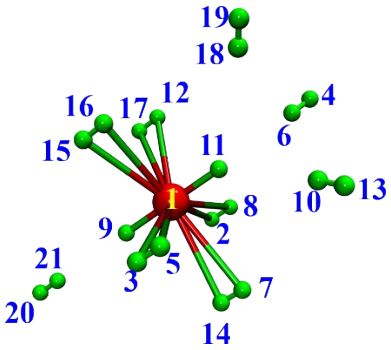
Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{18}	12(H)--13(H)	0.24404	-0.87800	1.00000	0.74535
	17(H)--16(H)	0.24493	-0.88369	1.00000	0.74382
	7(H)--2(H)	0.24501	-0.88420	1.00000	0.74368
	12(H)--1(Mg)	0.00303	0.00667	0.01894	3.1328
	13(H)--1(Mg)	0.00300	0.00664	0.01868	3.13541
	6(H)--14(H)	0.24407	-0.87821	1.00000	0.7453
	3(H)--15(H)	0.24405	-0.87808	1.00000	0.74533
	6(H)--1(Mg)	0.00294	0.00653	0.01818	3.14963
	3(H)--1(Mg)	0.00298	0.00660	0.01856	3.14032
	14(H)--1(Mg)	0.00294	0.00652	0.01816	3.14985
	8(H)--1(Mg)	0.05170	0.19636	0.13149	1.71441
	15(H)--1(Mg)	0.00298	0.00660	0.01852	3.14082
	1(Mg)--5(H)	0.05169	0.19632	0.13145	1.7145
	1(Mg)--10(H)	0.00288	0.00642	0.01767	3.163
	1(Mg)--4(H)	0.00291	0.00648	0.01796	3.15543
	1(Mg)--9(H)	0.00287	0.00641	0.01760	3.16398
	1(Mg)--11(H)	0.00291	0.00647	0.01792	3.15601
	10(H)--9(H)	0.24409	-0.87840	1.00000	0.74526
	4(H)--11(H)	0.24408	-0.87830	1.00000	0.74528
	18(H)--19(H)	0.24494	-0.88369	1.00000	0.74383

Table S5-14. MgH_{19}



Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{19}	18(H)--17(H)	0.24498	-0.88399	1.00000	0.74375
	15(H)--10(H)	0.24502	-0.88426	1.00000	0.74375
	14(H)--16(H)	0.24501	-0.88424	1.00000	0.74367
	2(H)--1(Mg)	0.05265	0.20086	0.13292	1.70298
	3(H)--7(H)	0.24264	-0.86825	1.00000	0.7474
	5(H)--1(Mg)	0.03918	0.14031	0.10840	1.82734
	1(Mg)--7(H)	0.00597	0.01446	0.02904	2.67832
	6(H)--4(H)	0.24264	-0.86824	1.00000	0.7474
	1(Mg)--4(H)	0.00597	0.01446	0.02904	2.67816
	5(H)--12(H)	0.05916	0.03354	0.62674	1.43852
	1(Mg)--12(H)	0.03918	0.14032	0.10839	1.82731
	20(H)--19(H)	0.24497	-0.88397	1.00000	0.74375
	13(H)--9(H)	0.24502	-0.88424	1.00000	0.74367
	11(H)--8(H)	0.24502	-0.88427	1.00000	0.74366

Table S5-15. MgH_{20}



Cluster	Connected atoms	ρ / a. u.	$\nabla^2\rho$ / a. u.	ELF	Atom distance / Å
MgH_{20}	16(H)--15(H)	0.24404	-0.87806	1.00000	0.74534
	5(H)--3(H)	0.24404	-0.87804	1.00000	0.74535
	13(H)--10(H)	0.24501	-0.88421	1.00000	0.74372
	16(H)--1(Mg)	0.00301	0.00665	0.01885	3.13615
	21(H)--20(H)	0.24493	-0.88365	1.00000	0.74372
	15(H)--1(Mg)	0.00298	0.00660	0.01847	3.13957
	5(H)--1(Mg)	0.00302	0.00666	0.01893	3.13385
	3(H)--1(Mg)	0.00299	0.00663	0.01858	3.13708
	19(H)--18(H)	0.24499	-0.88408	1.00000	0.74372
	9(H)--1(Mg)	0.05170	0.19640	0.13142	1.71442
	1(Mg)--17(H)	0.00294	0.00652	0.01822	3.15022
	1(Mg)--11(H)	0.05168	0.19614	0.13152	1.71464
	1(Mg)--12(H)	0.00292	0.00651	0.01803	3.15194
	17(H)--12(H)	0.24407	-0.87824	1.00000	0.7453
	1(Mg)--7(H)	0.00293	0.00650	0.01810	3.15315
	1(Mg)--14(H)	0.00291	0.00648	0.01788	3.1551
	7(H)--14(H)	0.24408	-0.87828	1.00000	0.74529
	1(Mg)--8(H)	0.00291	0.00646	0.01792	3.15879
	1(Mg)--2(H)	0.00287	0.00642	0.01756	3.16228
	8(H)--2(H)	0.24409	-0.87839	1.00000	0.74526
	6(H)--4(H)	0.24499	-0.88406	1.00000	0.74372

Bader proposed one kind of topology analysis technique to study electron density in "Atom-in-Molecular" (AIM) theory [S11]. The Multiwfn software makes it easy to perform calculations such as electron density (ρ), Laplacian of electron density ($\nabla^2\rho$) [S12] and electron localization function (ELF) [S13] on cluster bond critical points (BCPs), which can help us to study the nature of chemical bonds. According to the bond critical point topology property, the strength of the same chemical bond can be

compared by the magnitude of the electron density ρ, i.e. the higher the value of ρ, the stronger the bond. $\nabla^2\rho$(BCP) is a useful criterion for the type of chemical bond. When it is greater than 0, it means that the chemical bonding is in the form of non-covalent bonds, sometimes called closed-shell interactions, while the corresponding ELF value will be less than 0.5. And when it is less than zero, the corresponding chemical bonds are generally covalent bonds, and the ELF value will be greater than 0.5 at this time.

Reference

[S11] Bader, Richard FW. "Atoms in molecules." Accounts of Chemical Research 18.1 (1985): 9-15.

[S12] Lu, Tian, and Feiwu Chen. "Bond order analysis based on the Laplacian of electron density in fuzzy overlap space." The Journal of Physical Chemistry A 117.14 (2013): 3100-3108.

[S13] Becke, Axel D., and Kenneth E. Edgecombe. "A simple measure of electron localization in atomic and molecular systems." The Journal of chemical physics 92.9 (1990): 5397-5403.

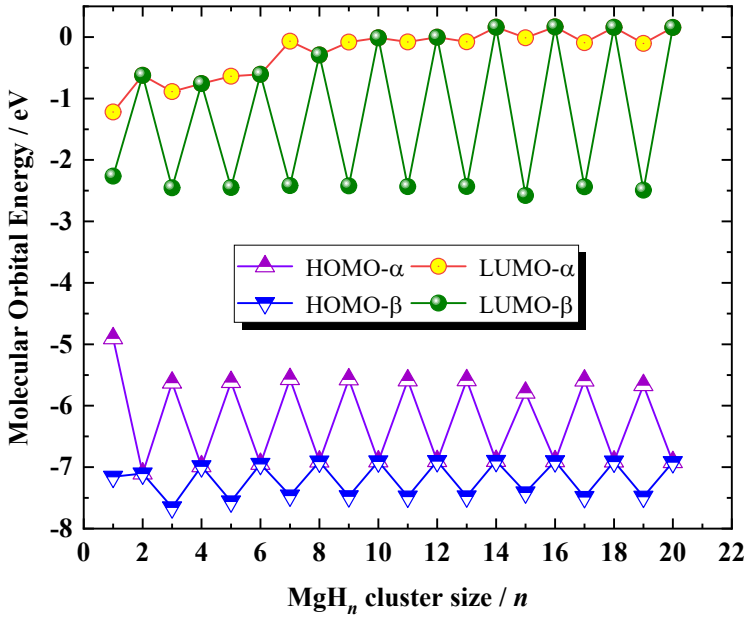


Figure S1. HOMO and LUMO molecular orbital energy of MgH_n (n=1-2) clusters.

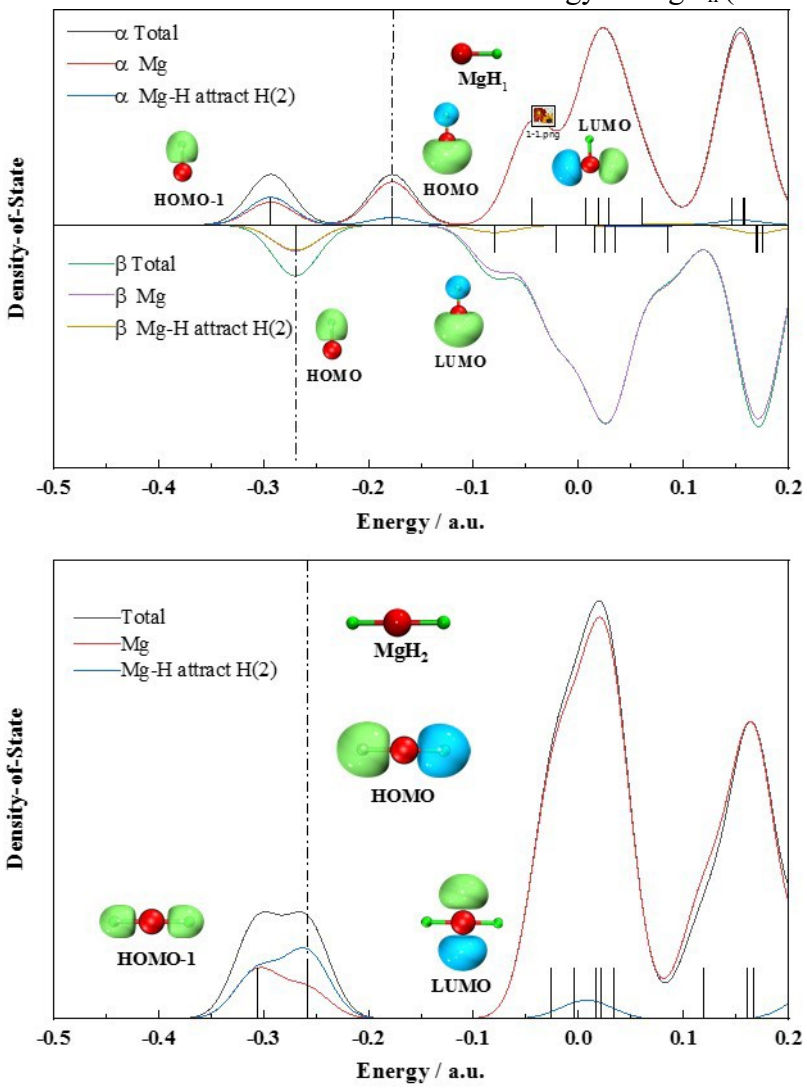


Figure S2-1. TDOS, PDOS and mol MOs diagram of MgH_n (n=1-2) clusters.

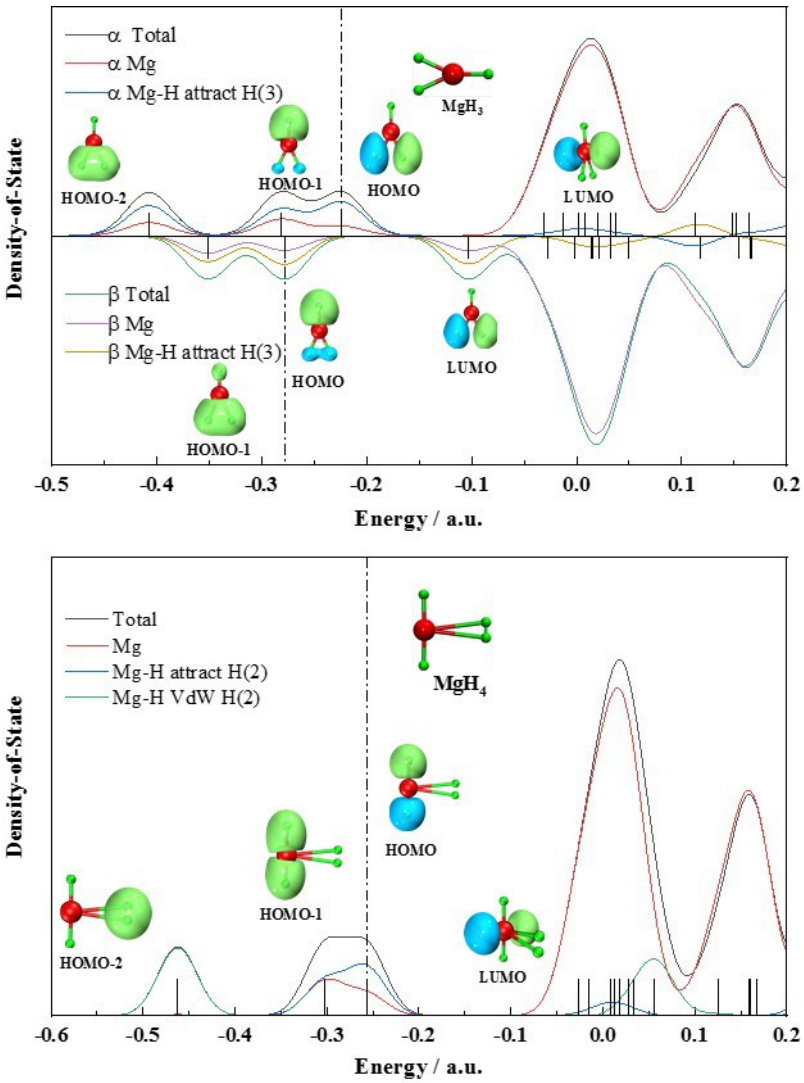


Figure S2-2. TDOS, PDOS and mol MOs diagram of MgH_n (n=3-4) clusters.

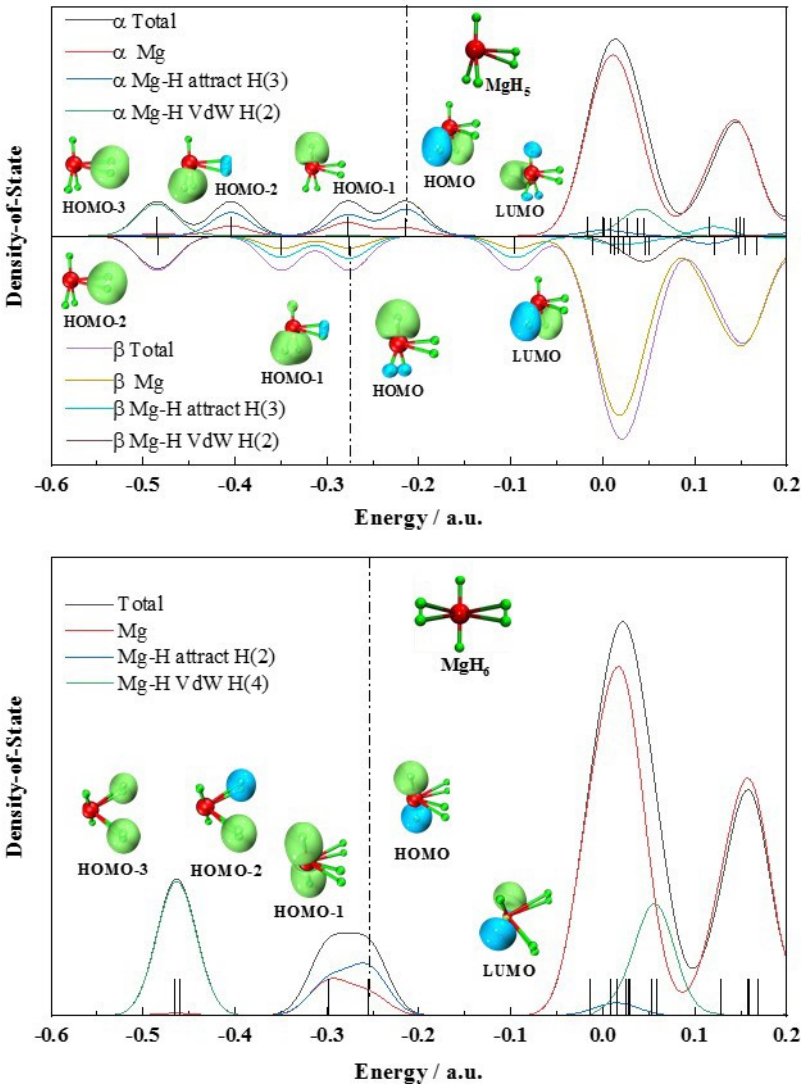


Figure S2-3. TDOS, PDOS and mol MOs diagram of MgH_n (n=5-6) clusters.

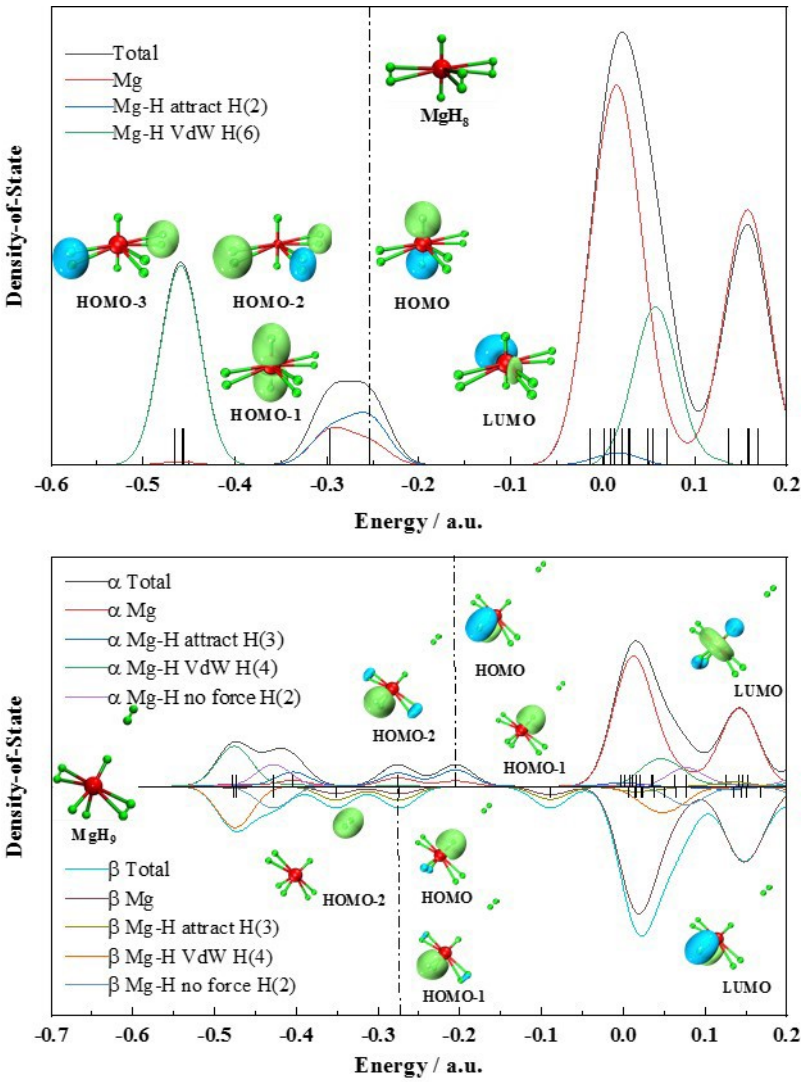


Figure S2-4. TDOS, PDOS and mol MOs diagram of MgH_n (n=8-9) clusters.

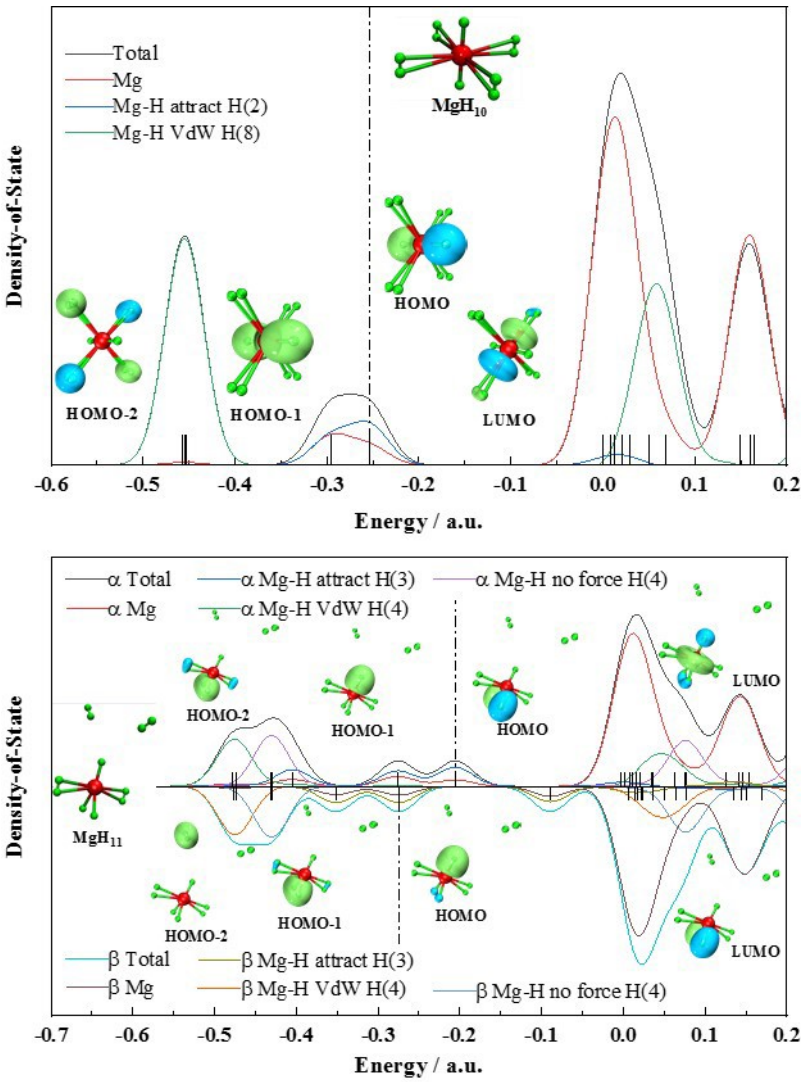


Figure S2-5. TDOS, PDOS and mol MOs diagram of MgH_n (n=10-11) clusters.

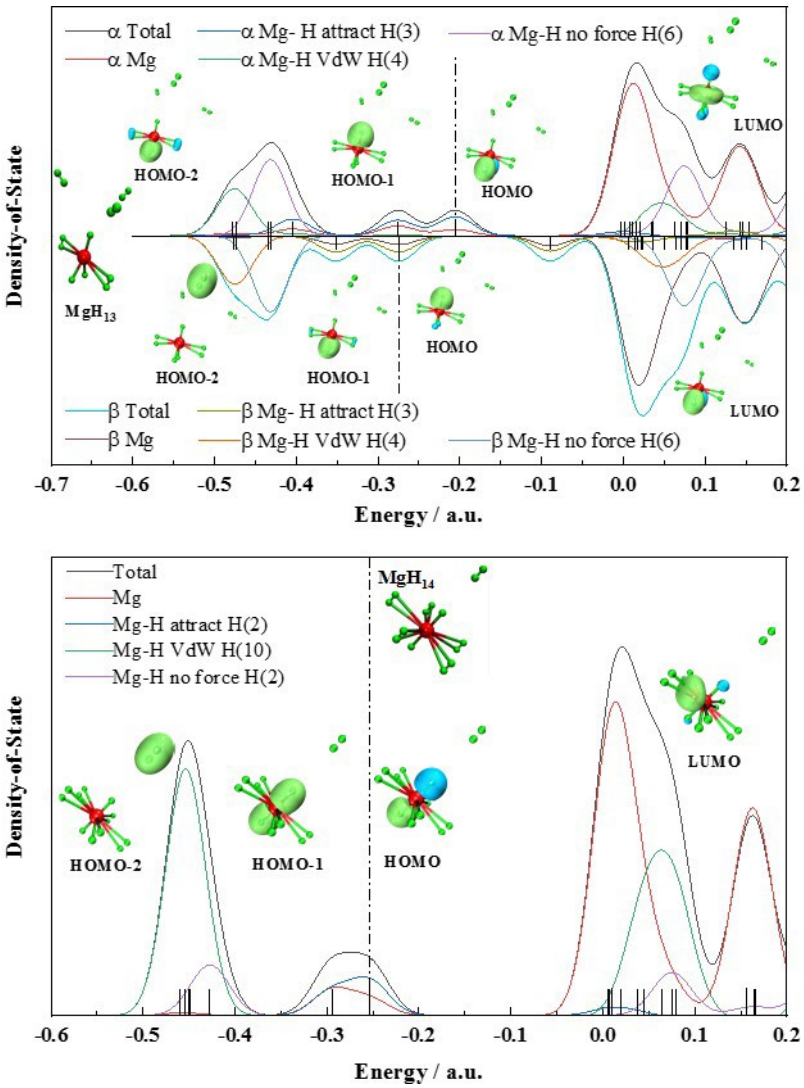


Figure S2-6. TDOS, PDOS and mol MOs diagram of MgH_n (n=13-14) clusters.

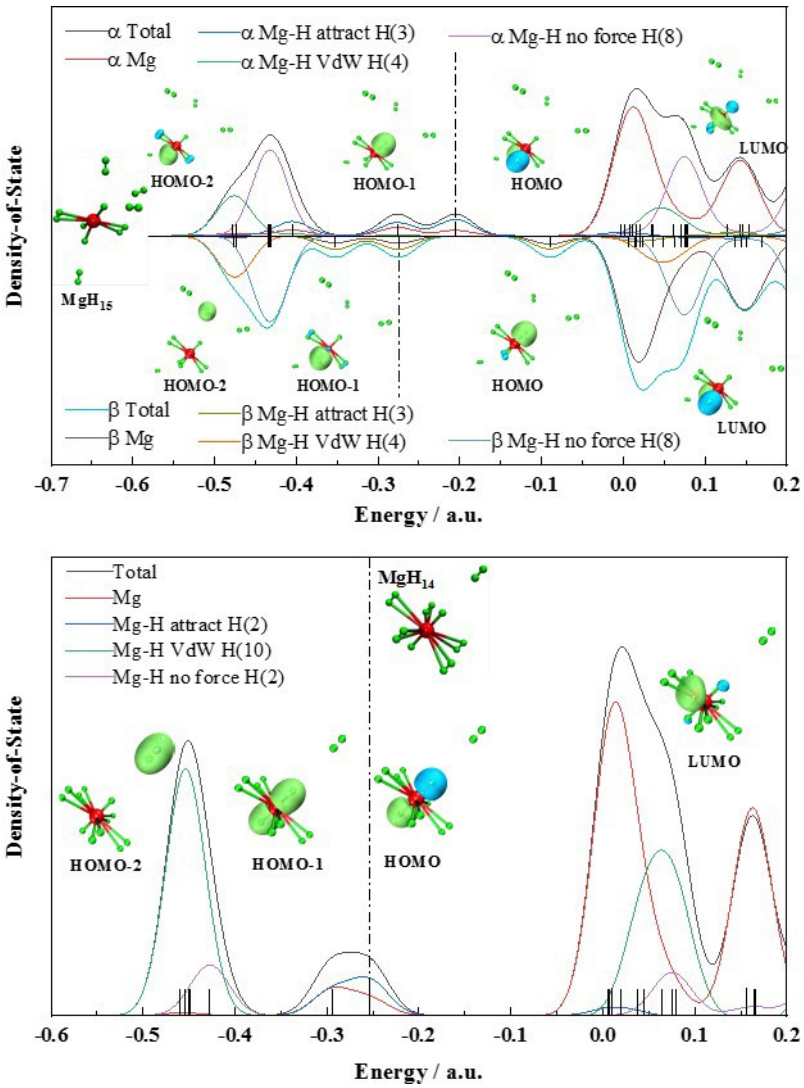


Figure S2-7. TDOS, PDOS and mol MOs diagram of MgH_n (n=15-16) clusters.

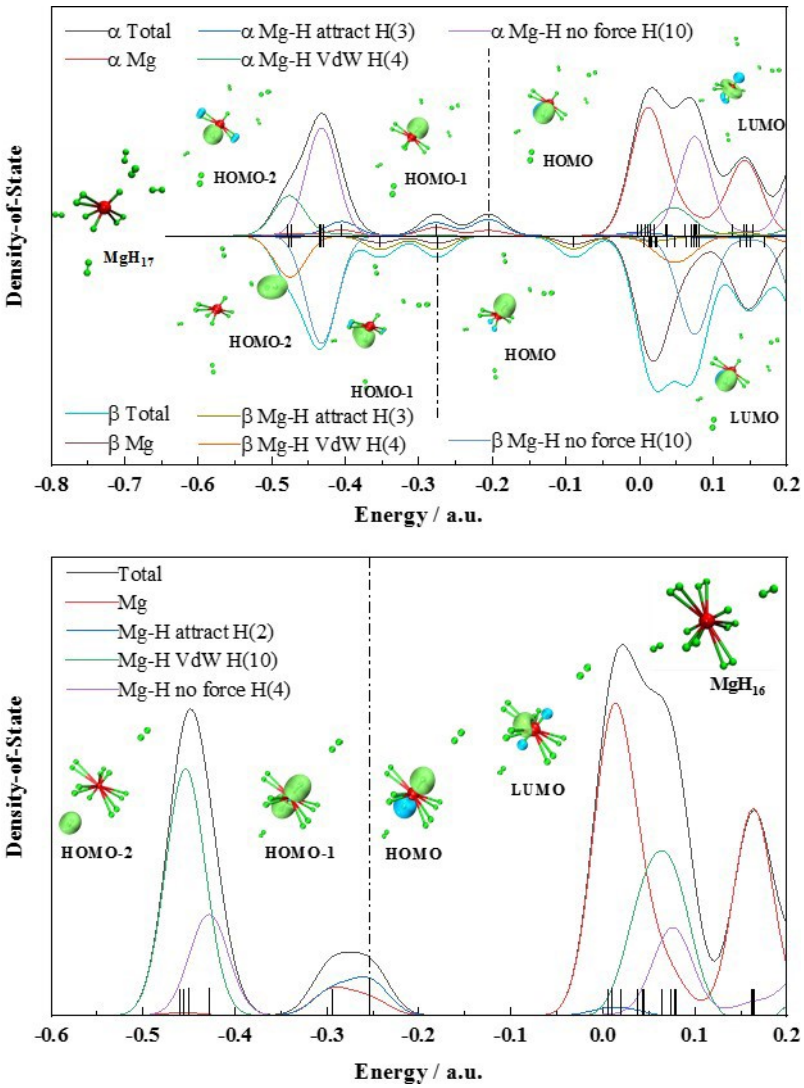


Figure S2-8. TDOS, PDOS and mol MOs diagram of MgH_n (n=17-18) clusters.

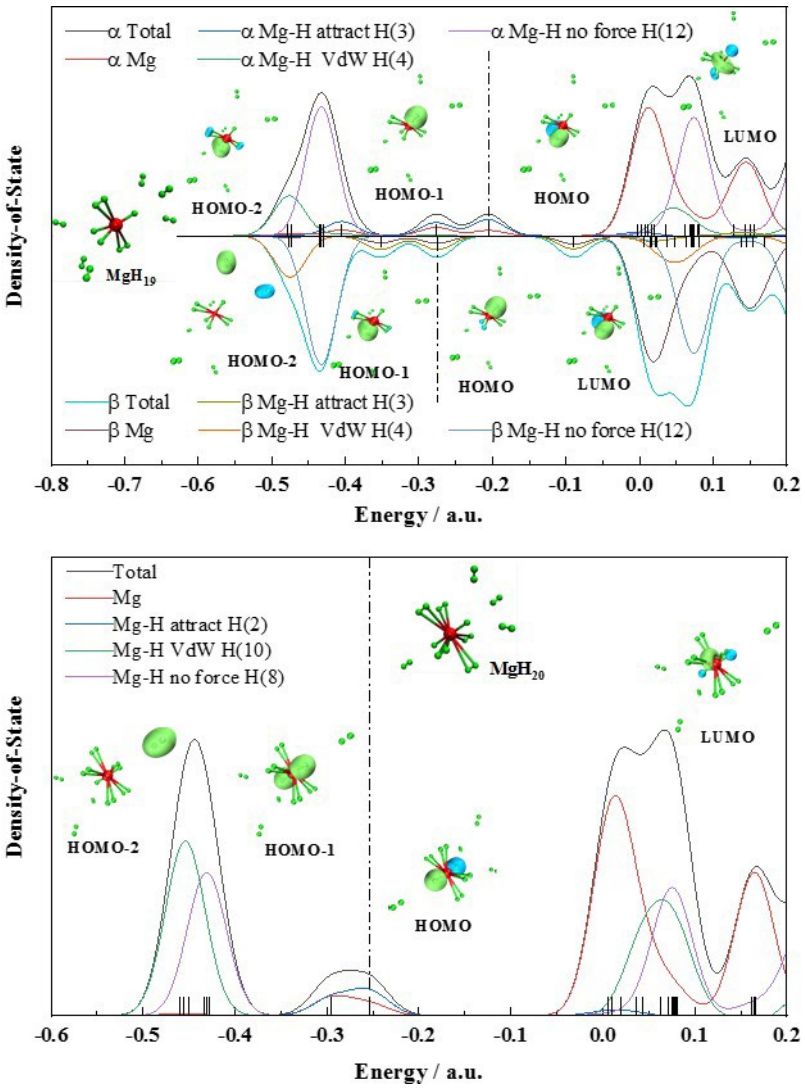


Figure S2-9. TDOS, PDOS and mol MOs diagram of MgH_n (n=19-20) clusters.

The density of states (DOS) of a cluster system is different from that of a periodic system. Because clusters are isolated systems with no k-point concept, their states are often referred to molecular orbitals and therefore the calculated orbital energy levels are discrete. By using Gaussian-type Gaussian functions in Multiwfn software to broaden the discrete orbital energies, the orbital energies of the clusters can be transformed into smooth continuous DOS curves, which are usually defined as total density of states (TDOS). Because the TDOS is derived from the contributions of all orbitals of all atoms, it is easy to break it down into several partial contributions to be studied separately, which is the motivation for the partial density of states (PDOS) introduced in the paper. Since this work discusses clusters of Mg adsorbing multiple H atoms, the study suggests that there are three possibilities for Mg-H interactions,

namely strong Mg-H attraction, weakly interacting Mg-H adsorption, and no significant Mg-H interactions. Therefore, in our work we define each MgH_n into four parts, namely the Mg atom, the H atom with a strong attraction to the Mg atom, the H atom with a weak interaction with the Mg atom (van der Waals), and the H atom with no interaction with the Mg atom [S14]. All molecular orbital maps in this work were made with VMD software [S15].

Reference

[S14] Specific TDOS and PDOS plot operations can be found in section 4.10.1 of the Multiwfn manual, which can be download directly online in the following website, http://sobereva.com/multiwfn/misc/Multiwfn_3.8_dev.pdf.

[S15] Humphrey, William, Andrew Dalke, and Klaus Schulten. "VMD: visual molecular dynamics." Journal of molecular graphics 14.1 (1996): 33-38.

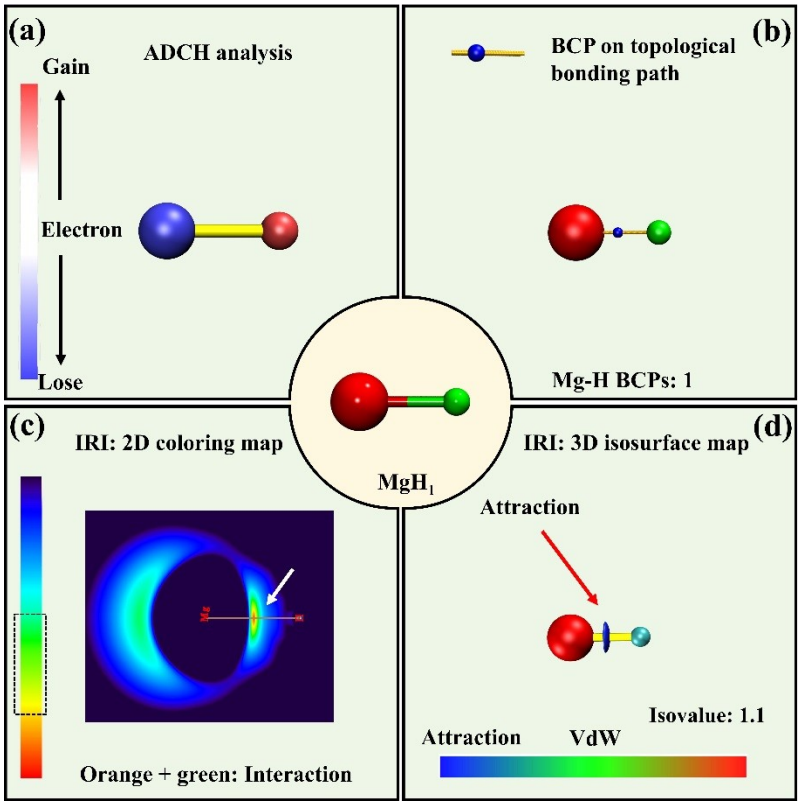


Figure S3-1. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_1 cluster.

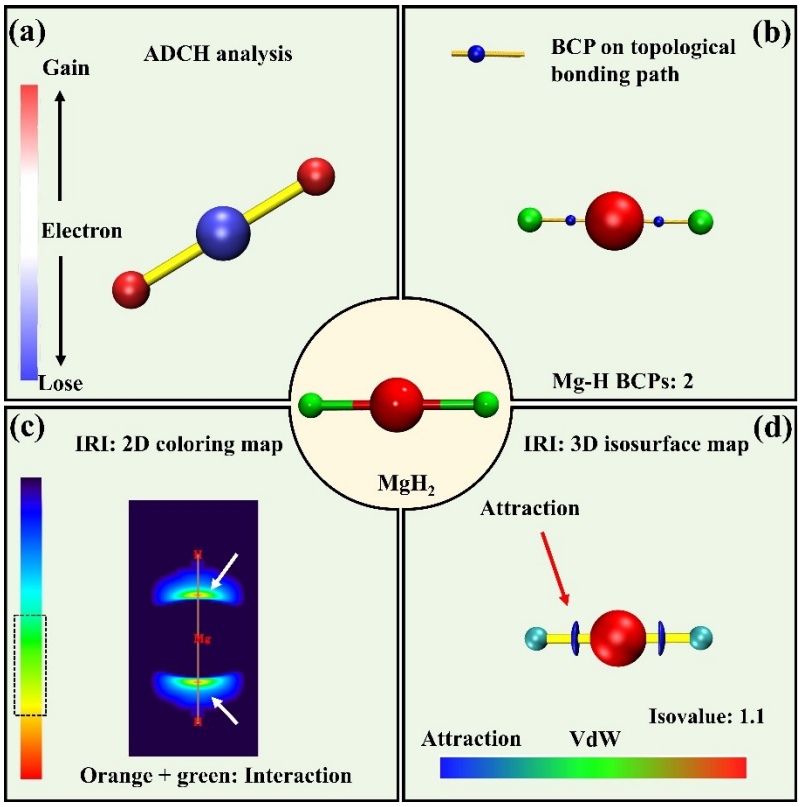


Figure S3-2. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_2 cluster.

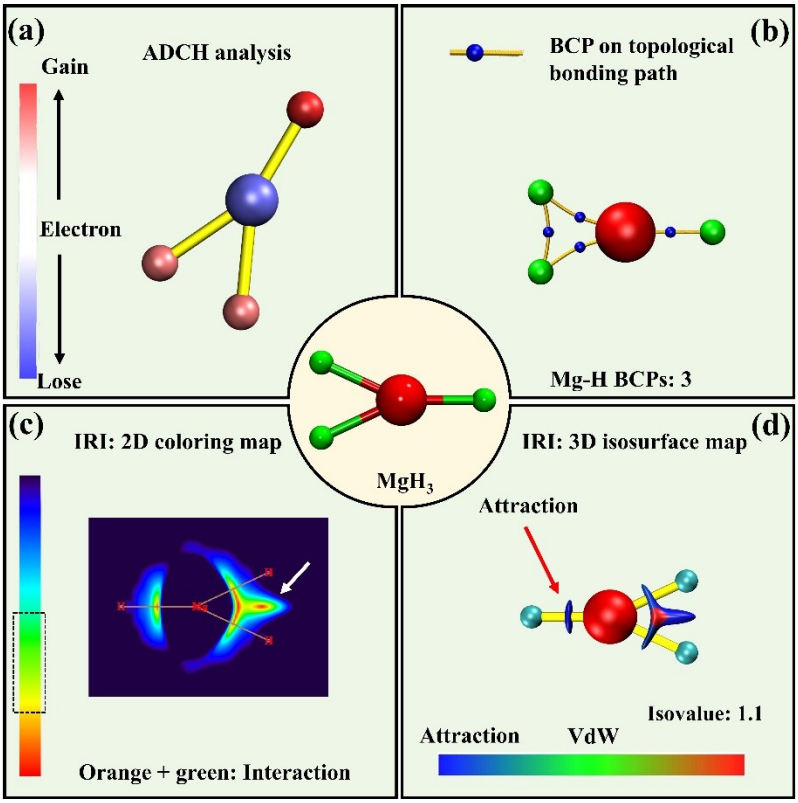


Figure S3-3. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_3 cluster.

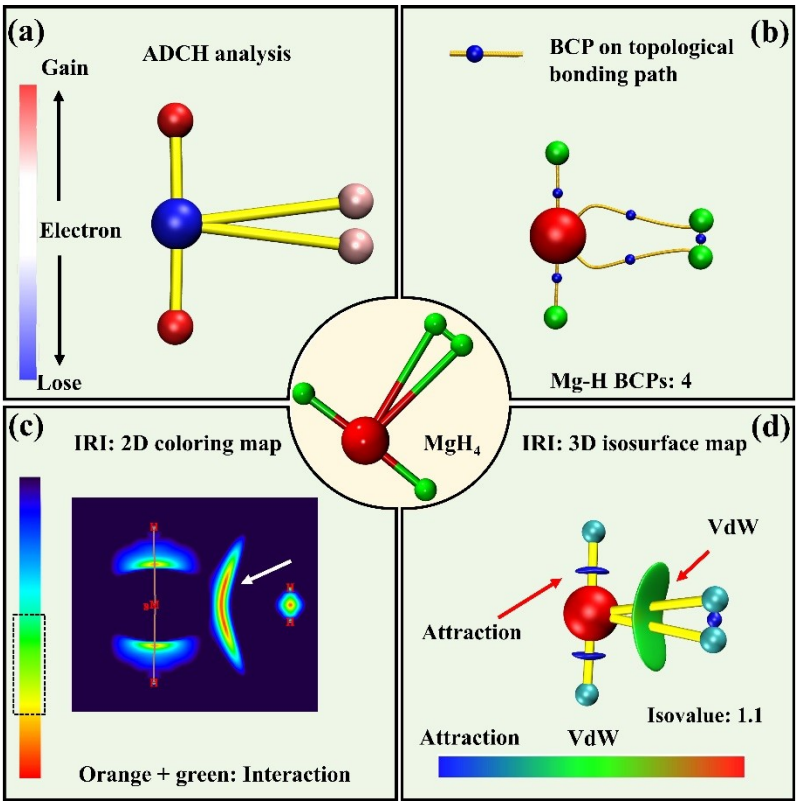


Figure S3-4. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_4 cluster.

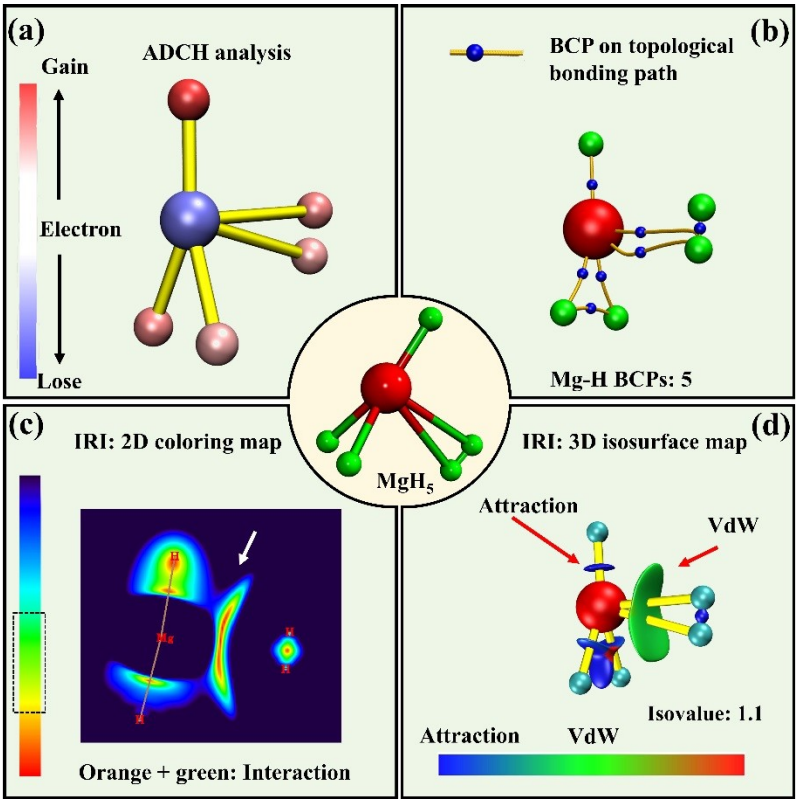


Figure S3-5. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_5 cluster.

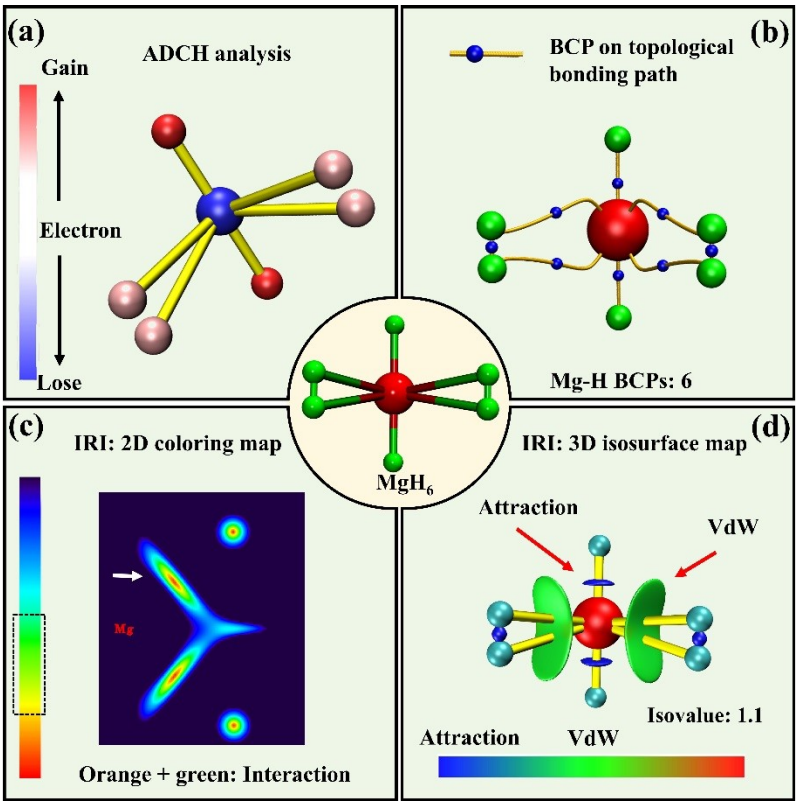


Figure S3-6. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_6 cluster.

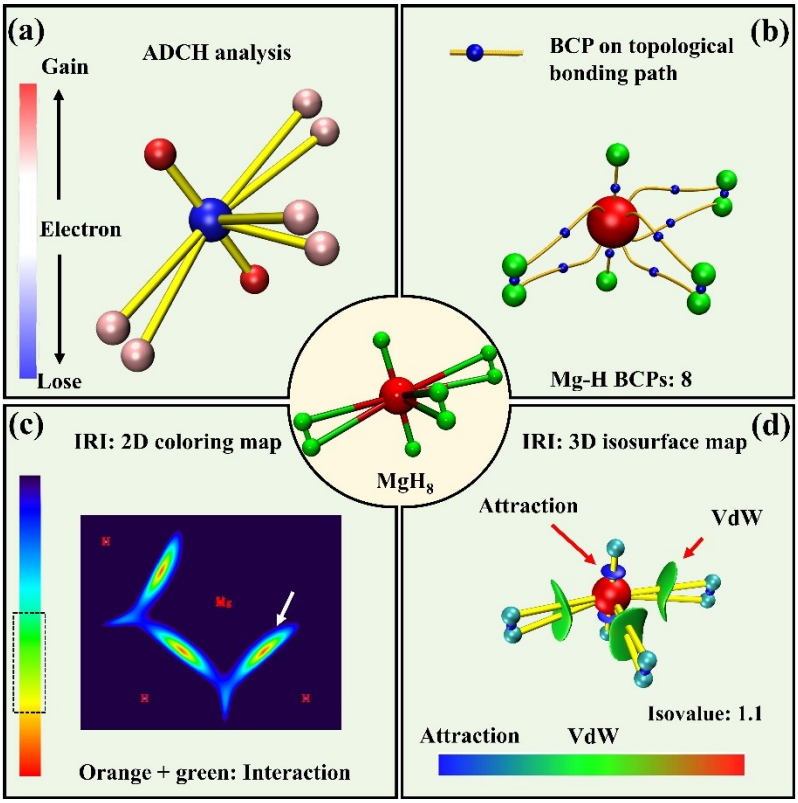


Figure S3-7. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_8 cluster.

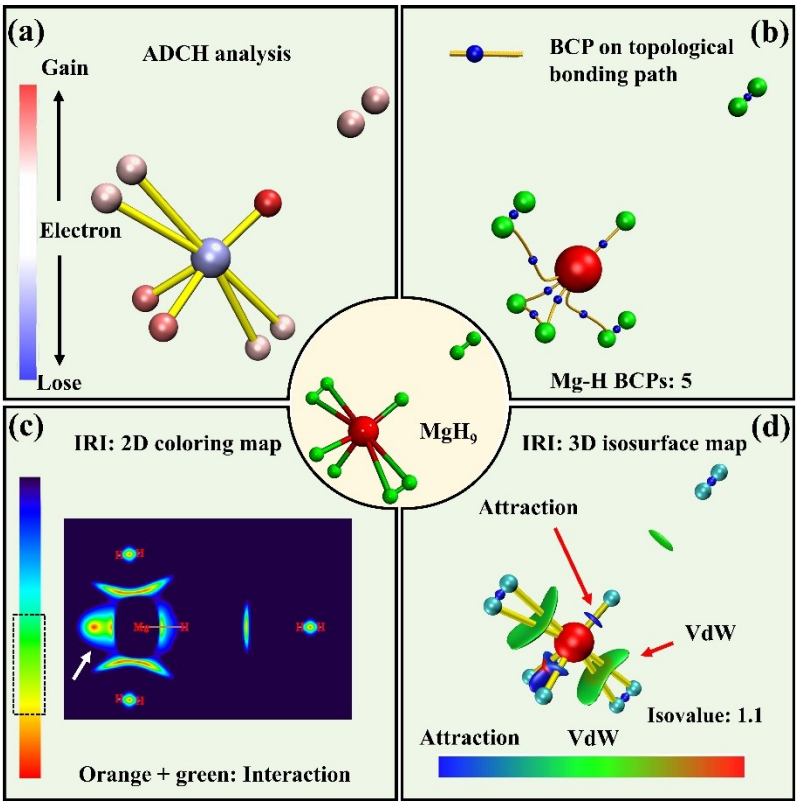


Figure S3-8. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_9 cluster.

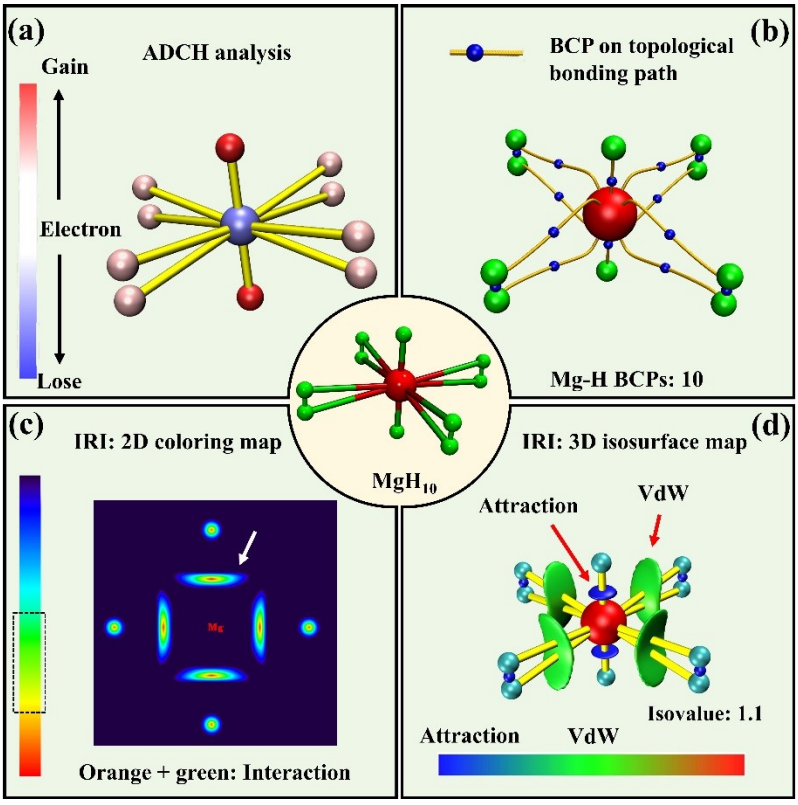


Figure S3-9. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{10} cluster.

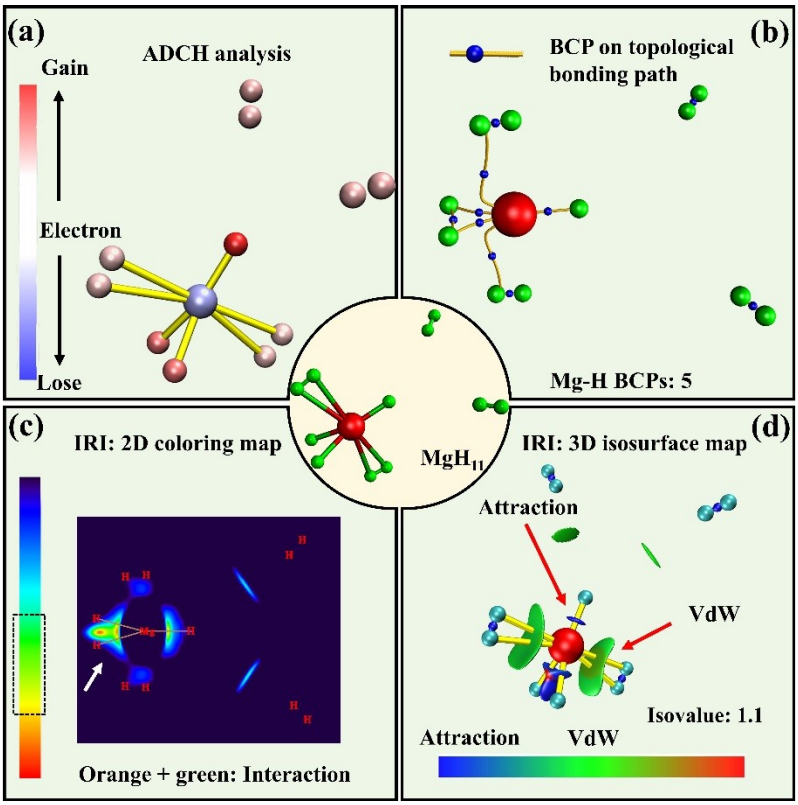


Figure S3-10. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{11} cluster.

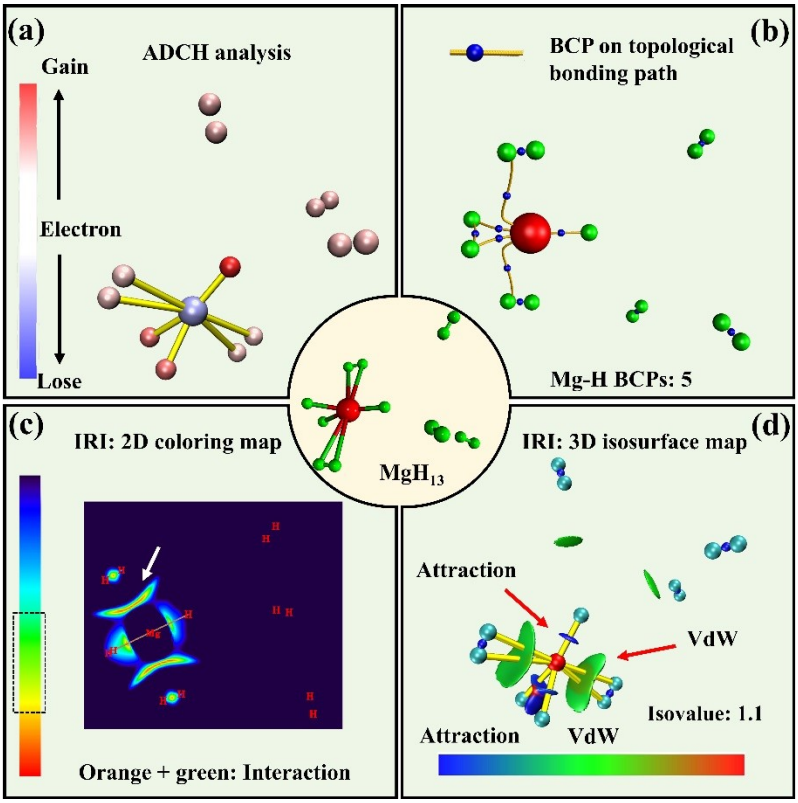


Figure S3-11. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{13} cluster.

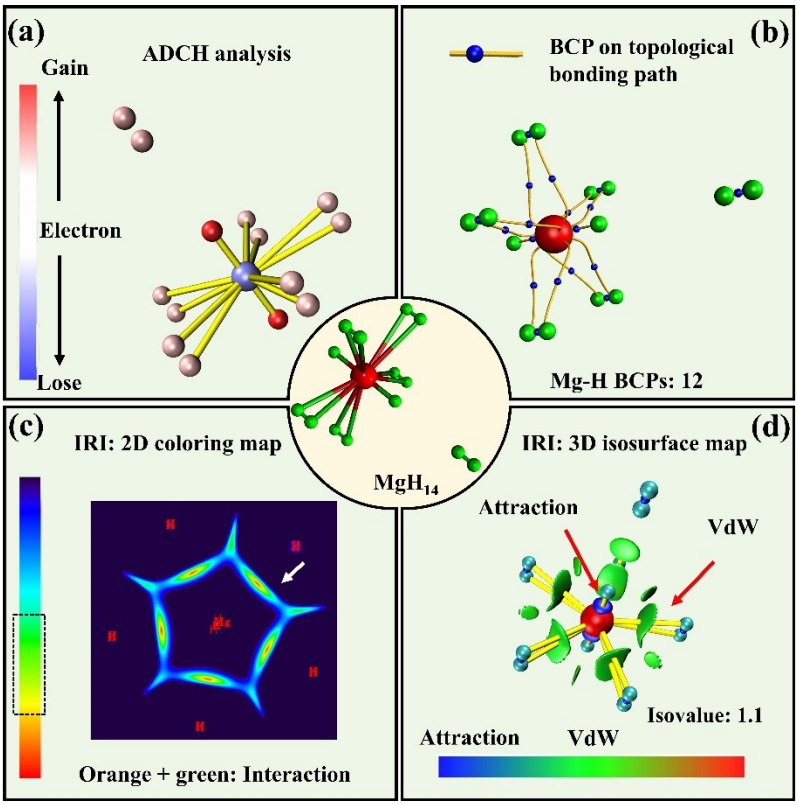


Figure S3-12. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{14} cluster.

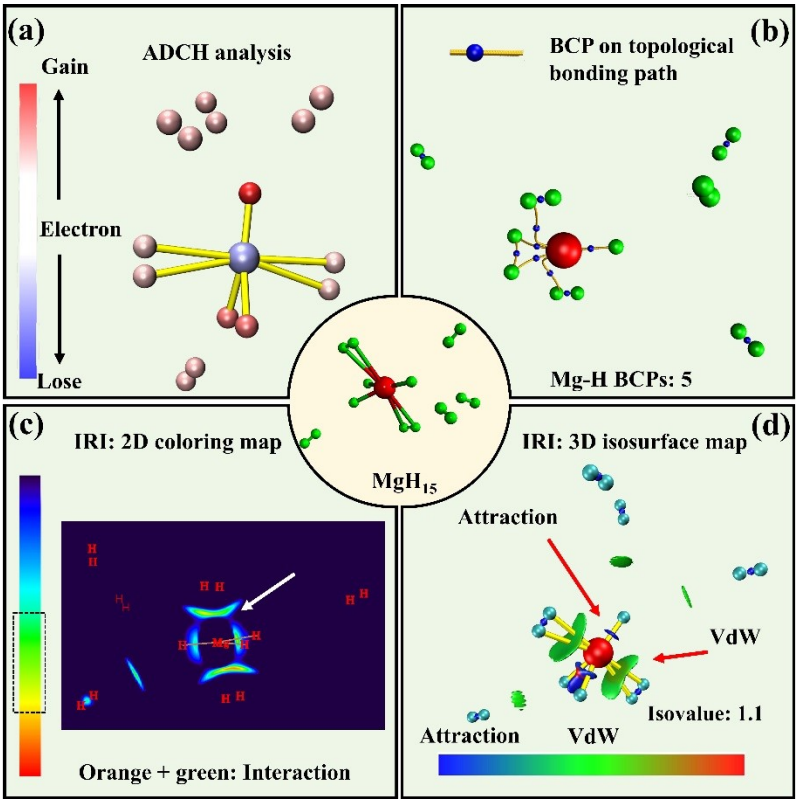


Figure S3-13. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{15} cluster.

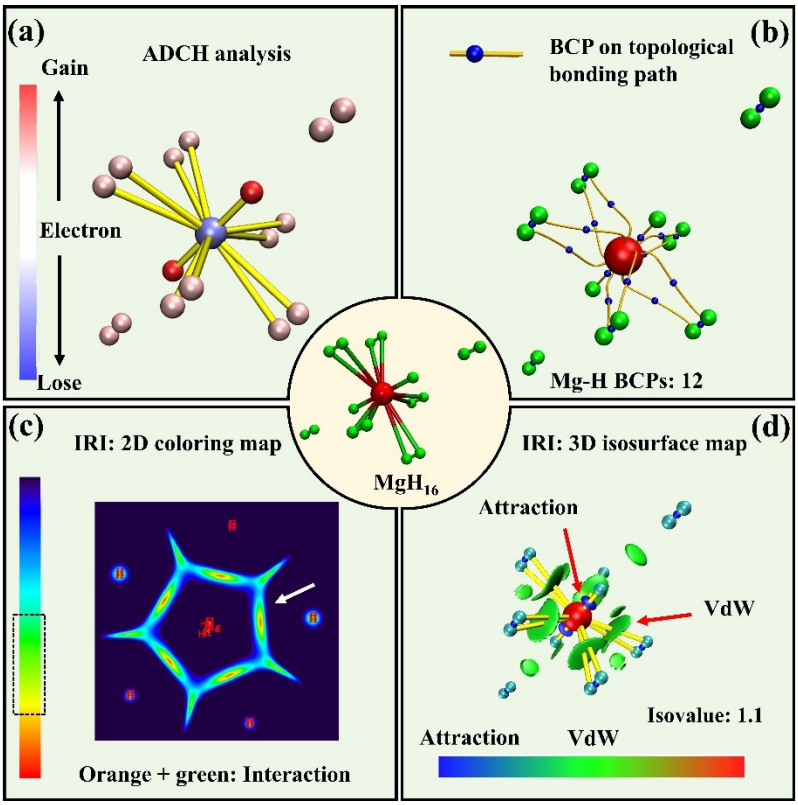


Figure S-14. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{16} cluster.

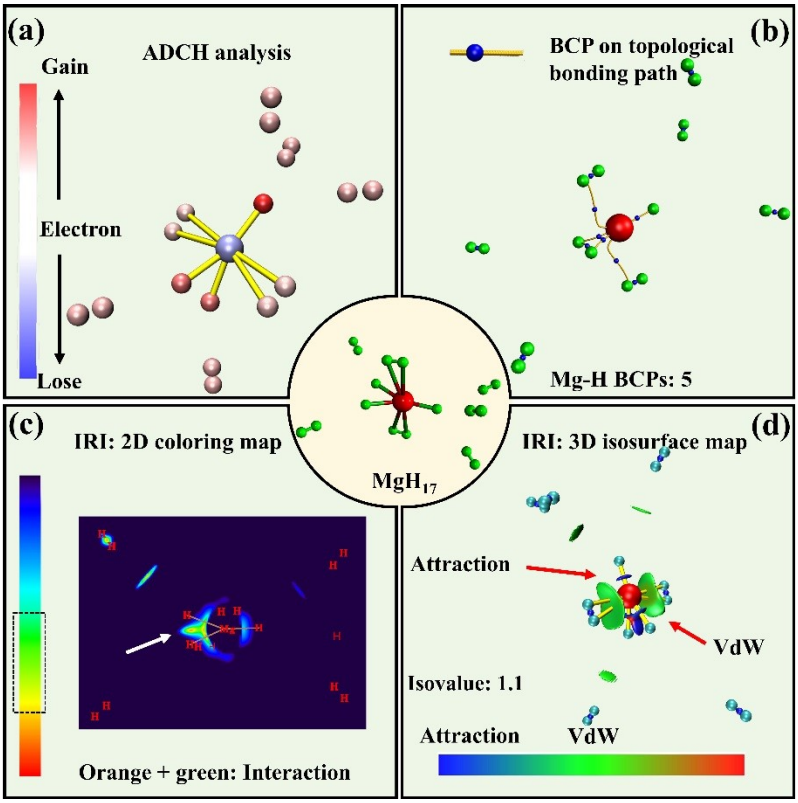


Figure S3-15. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{17} cluster.

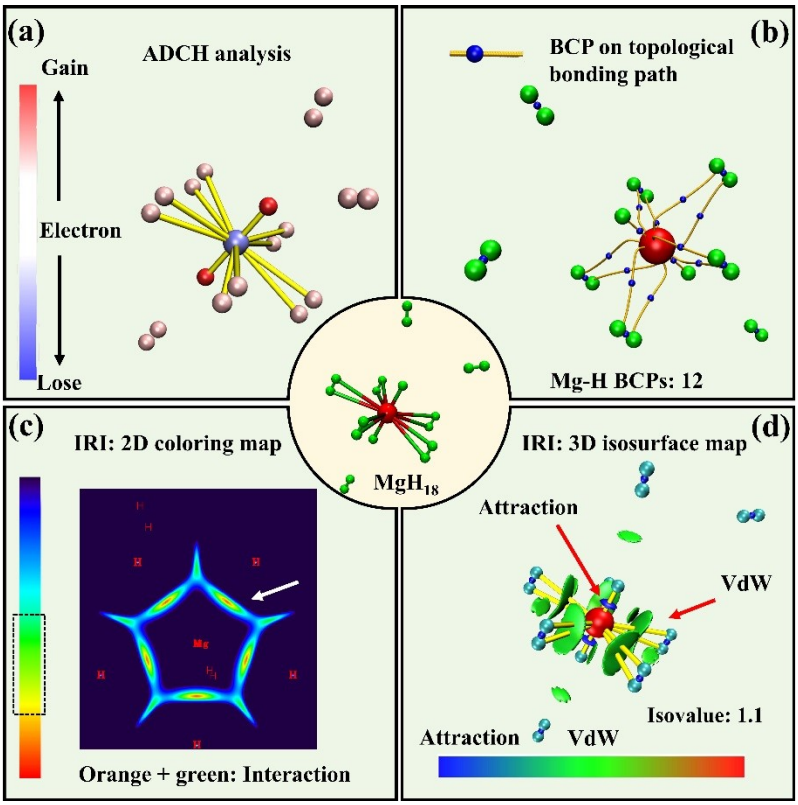


Figure S3-16. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{18} cluster.

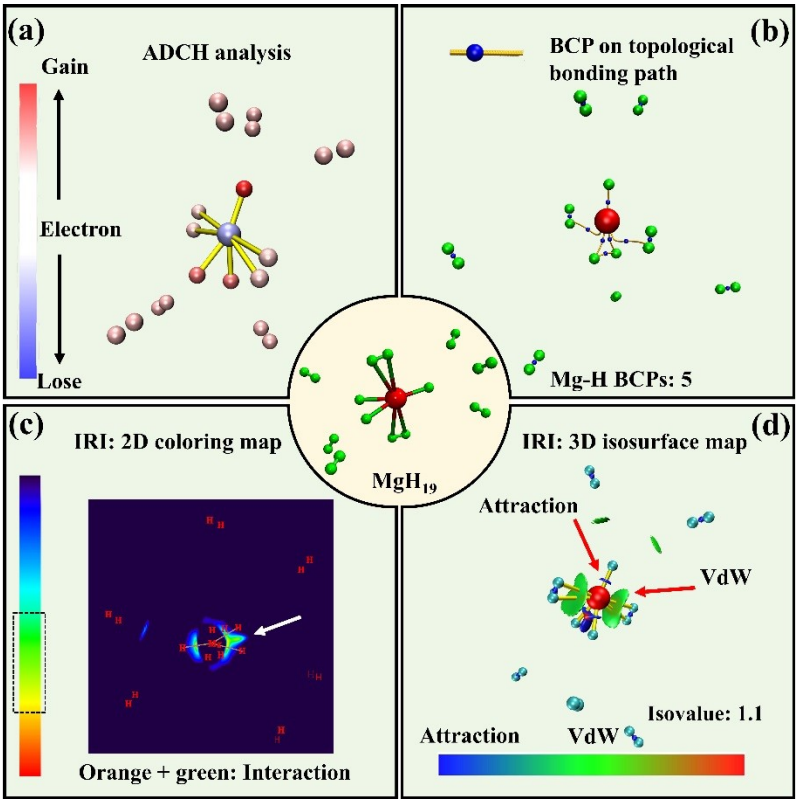


Figure S3-17. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{19} cluster.

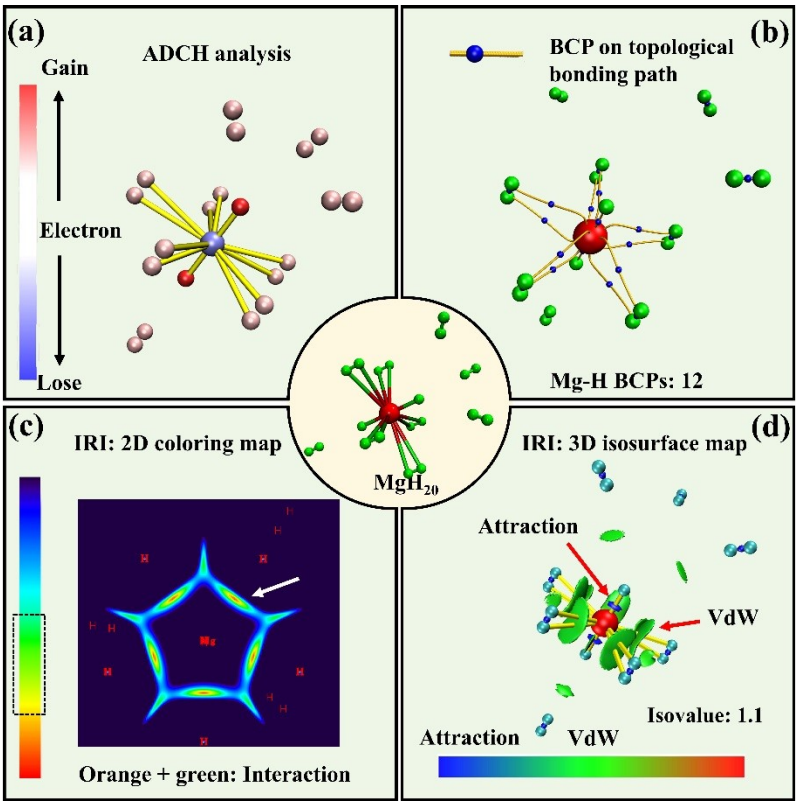


Figure S3-18. ADCH, BCP, IRI-2D and IRI-3D analysis for MgH_{20} cluster.

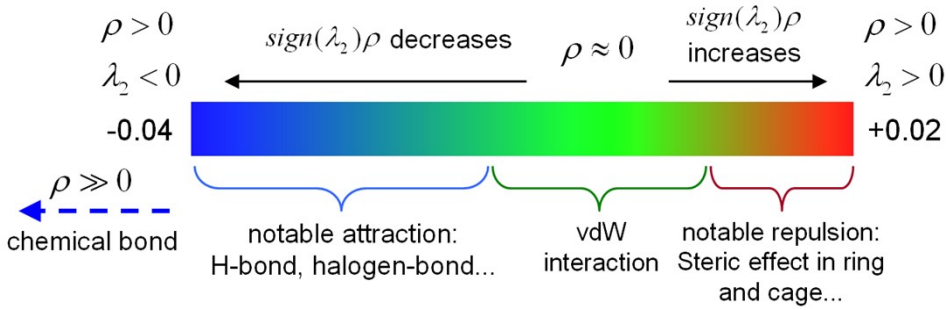


Figure S3-19. Illustration of IRI cooler-correspondence interactions

Figures 6(b), 7(b) in main text and Figures S3(b) show the BCPs bonding path [S16], which can be obtained through Multiwfn software together with VMD software. As shown in Figures 6(c-d), 7(c-d) in main text, and Figure S3 (c-d), We calculated and plotted the bonded and weakly interacting regions of the clusters using the Interaction region indicator (IRI) method [S17]. The key work of IRI is to distinguish the strength and character of the action of different regions by projecting the sign(λ_2)ρ function onto the IRI equivalent surface in different colors, where λ_2 represents the second largest eigenvalue of the electron density Hessian matrix, sign(λ_2) stands for taking the sign and ρ is the electron density. As displayed in **Figure S3-19**, the green color on the IRI equivalent surface indicates that this is a region of van der Waals interaction, or very weak dispersion-dominated hydrogen bonding, which is the force that allows some H_2 molecules to form relatively stable clusters despite the apparent absence of Mg atomic interactions.

The absence of red for all when IRI values in this study indicates that there is no site-blocking interaction in the MgH_n clusters. If the isosurface color is significantly blue, it means a significant attractive interaction, and if the isosurface is completely blue, it indicates either a relatively strong weak interaction here, so that the electron density (ρ) in the interaction region can reach ρ ≥ 0.04 a.u., or a chemical bonding interaction, where the electron density in the bonding region is usually significantly greater than ρ >> 0.04 a.u. There are three electron densities for BCPs in Figure S5, ρ(BCP) ~ 0.2 for H-H of H_2 molecules away from the Mg atom, and the blue region of H-H in Figure S3 for bonding. Some of the Mg-H in the odd and even MgH_n clusters have ρ(BCP) ~ 0.04, with ELF < 0.5 indicating apparent attractive interactions, while

some other Mg-H are apparent f van der Waals interactions, which have ρ(BCP) ~ 0.003. The above findings suggest that the two Mg-H, attractive bonding and VdW interactions defined in this study, and H-H bonding in H_2 molecules can indeed be confirmed by IRI-2D and IRI-3D [S18].

Reference

[S16] Specific BCPs bonding path search and plot can be found in section 4.2.1 of the Multiwfn manual, which can be directly download online in the following website, http://sobereva.com/multiwfn/misc/Multiwfn_3.8_dev.pdf.

[S17] Lu, Tian, and Qinxue Chen. "Interaction region indicator: A simple real space function clearly revealing both chemical bonds and weak interactions." Chemistry‐Methods 1.5 (2021): 231-239.

[S18] Specific IRI plot operations can be found in section 4.20.4 of the Multiwfn manual, which can be directly download online in the following website, http://sobereva.com/multiwfn/misc/Multiwfn_3.8_dev.pdf.