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Predicting bond dissociation energy and bond length for bimetallic diatomic molecules: A challenge for electronic structure theory

Junwei Lucas Bao,[2] Xin Zhang,[1,2,a)] Xuefei Xu,[3] and Donald G. Truhlar[2,b)]

[1]*State Key Laboratory of Chemical Resource Engineering, Institute of Materia Medica, College of Science, Beijing University of Chemical Technology, Beijing, 100029, P.R. China*

[2]*Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States*

[3]*Center for Combustion Energy, Tsinghua University, Beijing 100084, China*

[a)] zhangxin@mail.buct.edu.cn

[b)] truhlar@umn.edu

This supporting information contains full versions of Tables 4-9.

Table S1. The signed errors and mean unsigned errors (MUEs) for the calculated equilibrium bond length (re in the units of Å) for various XC functionals, using the ECP protocol.

Functional	Cr_2	V_2	Mo_2	VCr	VNb	ScCo	YCo	NbCr	MUE
BLYP	-0.083	-0.040	-0.007	-0.055	-0.019	-0.028	-0.001	0.003	0.029
MN12-L	-0.100	-0.019	-0.021	0.064	-0.008	-0.011	-0.002	0.048	0.034
MGGA_MS1	-0.106	-0.031	-0.031	0.003	-0.034	-0.045	-0.026	0.012	0.036
RPBE	-0.092	-0.048	-0.021	-0.004	-0.031	-0.037	-0.012	-0.049	0.037
SOGGA11	-0.100	-0.053	-0.041	-0.015	-0.042	-0.035	-0.006	-0.004	0.037
revPBE	-0.093	-0.050	-0.022	-0.006	-0.032	-0.039	-0.015	-0.049	0.038
MGGA_MS2	-0.103	-0.037	-0.026	-0.043	-0.030	-0.044	-0.021	0.012	0.039
PBE	-0.096	-0.054	-0.025	-0.068	-0.037	-0.046	-0.024	-0.004	0.044
MOHLYP	-0.101	-0.057	-0.035	0.011	-0.042	-0.041	-0.013	-0.058	0.045
MGGA_MS0	-0.107	-0.106	-0.031	0.012	-0.032	-0.045	-0.026	0.017	0.047
OreLYP	-0.108	-0.066	-0.040	-0.013	-0.051	-0.060	-0.037	-0.005	0.048
M06-L	-0.106	-0.061	-0.046	0.005	-0.044	-0.054	-0.039	0.027	0.048
OLYP	-0.109	-0.067	-0.041	-0.019	-0.053	-0.059	-0.037	-0.005	0.049
MGGA_MS2h	-0.117	-0.119	-0.041	0.012	-0.032	-0.056	-0.037	0.011	0.053
PBEsol	-0.105	-0.064	-0.034	-0.044	-0.049	-0.064	-0.045	-0.029	0.054
SOGGA	-0.107	-0.066	-0.037	-0.043	-0.051	-0.066	-0.048	-0.027	0.056
τ-HCTH	-0.117	-0.076	-0.046	-0.029	-0.062	-0.072	-0.049	-0.013	0.058
N12	-0.106	-0.132	-0.037	-0.043	-0.053	-0.062	-0.043	-0.059	0.067
N12-SX	-0.119	-0.077	-0.049	-0.041	-0.064	-0.063	-0.053	-0.067	0.067
B1LYP	-0.127	-0.135	-0.050	0.030	-0.077	-0.065	-0.048	-0.015	0.068
M11-L	-0.125	-0.099	-0.048	-0.097	-0.048	-0.076	-0.042	-0.061	0.075
O3LYP	-0.127	-0.083	-0.057	-0.054	-0.069	-0.076	-0.057	-0.085	0.076
MN15-L	-0.130	-0.080	-0.065	0.062	-0.068	-0.070	-0.062	0.076	0.077
B97-3	-0.140	-0.093	-0.065	-0.019	-0.076	-0.078	-0.062	-0.083	0.077
B3LYP	-0.121	-0.132	-0.044	-0.078	-0.065	-0.063	-0.044	-0.067	0.077
B97-1	-0.127	-0.082	-0.051	-0.098	-0.065	-0.067	-0.049	-0.083	0.078
τ-HCTHhyb	-0.122	-0.132	-0.047	-0.080	-0.062	-0.068	-0.050	-0.073	0.079
MPW3LYP	-0.124	-0.134	-0.047	-0.094	-0.059	-0.065	-0.048	-0.068	0.080
M05	-0.141	-0.150	-0.080	0.026	-0.132	-0.075	-0.051	-0.012	0.083
M06	-0.135	-0.145	-0.064	-0.057	-0.133	-0.078	-0.058	0.003	0.084
SOGGA11-X	-0.159	-0.015	-0.084	-0.077	-0.047	-0.092	-0.082	-0.118	0.084
MN12-SX	-0.120	-0.118	-0.041	0.276	-0.039	-0.038	-0.028	-0.067	0.091
TPSSh	-0.112	-0.126	-0.040	0.282	-0.046	-0.057	-0.038	-0.060	0.095
ωB97X-D	-0.144	-0.100	-0.077	-0.102	-0.086	-0.081	-0.067	-0.186	0.106
MPW1K	-0.165	-0.172	-0.089	-0.093	0.053	-0.097	-0.087	-0.123	0.110
M08-SO	-0.167	-0.180	-0.084	0.021	-0.186	-0.079	-0.060	-0.126	0.113
M11	-0.162	-0.182	-0.093	-0.122	-0.115	-0.077	-0.060	-0.119	0.116
MN15	-0.149	-0.166	-0.069	-0.183	-0.168	-0.094	-0.069	-0.035	0.116
ωB97X	-0.154	-0.160	-0.091	-0.122	-0.098	-0.088	-0.072	-0.196	0.123
HSE06	-0.136	-0.148	-0.062	0.011	-0.101	-0.077	-0.063	0.479	0.135

PW6B95	-0.062	-0.058	-0.063	0.695	-0.068	-0.150	-0.063	-0.039	0.150
GAM	-0.116	-0.073	-0.052	0.714	-0.055	-0.057	-0.032	0.114	0.152
MPW1B95	-0.146	-0.064	-0.071	0.728	-0.068	-0.093	-0.072	-0.043	0.161
PBE0	-0.139	-0.152	-0.065	0.761	-0.059	-0.082	-0.068	-0.084	0.176
MPWB1K	-0.070	-0.116	-0.089	0.838	-0.006	-0.148	-0.087	0.073	0.178
M06-2X	-0.174	-0.186	-0.091	0.834	-0.036	-0.111	-0.099	-0.134	0.208
M05-2X	-0.176	-0.180	-0.089	0.735	-0.183	-0.108	-0.091	-0.130	0.211
M08-HX	-0.172	-0.180	-0.087	0.812	0.334	-0.088	-0.077	-0.122	0.234
PWB6K	-0.167	-0.117	-0.090	0.848	0.014	-0.147	-0.086	0.677	0.268
M06-HF	-0.214	-0.160	-0.111	0.940	0.132	-0.102	-0.108	0.892	0.332
Exptl. r_e	1.681	1.770	1.938	1.724	1.943	1.809	1.980	1.892	–

Table S2. The signed errors and mean unsigned errors (MUEs) for the calculated equilibrium bond length (r_e in the units of Å) for various XC functionals, using the DKH protocol.

Functional	Cr_2	V_2	Mo_2	VCr	VNb	ScCo	YCo	NbCr	MUE
BLYP	0.003	-0.018	-0.003	-0.015	-0.006	-0.005	0.007	0.000	0.007
RPBE	-0.085	-0.024	-0.020	0.006	-0.017	-0.011	-0.005	0.013	0.023
revPBE	-0.087	-0.026	-0.021	0.000	-0.019	-0.014	-0.008	0.012	0.024
SOGGA11	0.028	-0.021	-0.040	-0.039	-0.067	0.002	0.003	0.002	0.025
PBE	-0.092	-0.033	-0.024	-0.023	-0.025	-0.025	-0.018	-0.005	0.031
MOHLYP	-0.095	-0.032	-0.035	0.062	-0.028	-0.010	-0.006	-0.036	0.038
OLYP	0.096	-0.048	-0.043	-0.012	-0.042	-0.037	-0.032	-0.001	0.039
OreLYP	0.120	-0.048	-0.042	-0.009	-0.041	-0.038	-0.033	-0.004	0.042
PBEsol	-0.105	-0.049	-0.036	-0.053	-0.040	-0.048	-0.042	-0.008	0.048
MGGA_MS0	-0.106	-0.109	-0.039	0.009	-0.035	-0.035	-0.040	0.018	0.049
SOGGA	-0.107	-0.051	-0.040	-0.052	-0.043	-0.050	-0.045	-0.032	0.053
τ-HCTH	-0.122	-0.066	-0.050	-0.024	-0.056	-0.057	-0.047	-0.009	0.054
N12-SX	-0.038	-0.067	-0.040	-0.030	-0.124	-0.052	-0.044	-0.054	0.056
M11-L	-0.004	-0.142	-0.065	-0.036	-0.040	-0.073	-0.050	-0.057	0.058
MN12-L	-0.015	-0.072	-0.049	-0.096	-0.058	-0.062	-0.053	-0.062	0.058
N12	-0.111	-0.059	-0.044	-0.080	-0.051	-0.054	-0.043	-0.069	0.064
MGGA_MS1	-0.105	-0.109	-0.038	0.158	-0.034	-0.033	-0.037	0.016	0.066
M06-L	-0.107	-0.044	-0.046	0.178	-0.034	-0.034	-0.030	0.060	0.067
B97-3	-0.142	-0.081	-0.065	-0.011	-0.067	-0.058	-0.056	-0.173	0.082
MN12-SX	-0.139	-0.020	-0.057	0.393	-0.097	-0.054	-0.052	0.006	0.102
PW6B95	-0.141	-0.043	-0.063	-0.008	-0.096	-0.061	-0.058	0.367	0.105
SOGGA11-X	-0.164	-0.104	-0.083	-0.128	-0.039	-0.075	-0.075	-0.189	0.107
M05	-0.141	-0.077	-0.078	-0.171	-0.091	-0.040	-0.039	0.263	0.112
MGGA_MS2	0.677	0.000	-0.035	-0.051	-0.031	-0.029	-0.033	-0.040	0.112
ωB97X-D	0.155	-0.091	-0.078	-0.182	-0.081	-0.065	-0.063	-0.181	0.112
M06	-0.136	-0.136	-0.056	-0.167	-0.081	-0.049	-0.041	0.316	0.123
PBE0	-0.142	-0.150	-0.065	-0.181	-0.147	-0.065	-0.063	-0.176	0.124
MGGA_MS2h	-0.118	-0.120	-0.049	0.008	-0.095	-0.043	-0.048	0.515	0.125
B3LYP	-0.123	-0.129	-0.042	-0.162	-0.125	-0.046	-0.038	0.413	0.135
τ-HCTHhyb	0.566	-0.068	-0.050	0.086	-0.096	-0.054	-0.050	-0.160	0.141
TPSSh	0.739	-0.124	-0.042	-0.072	-0.040	-0.041	-0.038	-0.058	0.144
GAM	-0.118	-0.057	-0.058	0.818	-0.045	-0.035	-0.025	-0.044	0.150
O3LYP	-0.129	-0.070	-0.058	0.670	-0.116	-0.057	-0.053	-0.169	0.165
ωB97X	0.749	-0.102	-0.048	-0.039	-0.137	-0.071	-0.068	-0.145	0.170
B1LYP	0.831	-0.026	-0.047	-0.166	-0.048	-0.048	-0.041	-0.159	0.171
MN15-L	0.754	-0.080	-0.078	-0.104	-0.074	-0.070	-0.076	0.211	0.181
B97-1	0.709	-0.043	-0.053	-0.168	-0.133	-0.050	-0.048	0.315	0.190
M08-SO	-0.167	-0.165	-0.082	0.788	-0.040	-0.043	-0.045	-0.190	0.190
M05-2X	-0.174	-0.114	-0.086	0.699	-0.096	-0.081	-0.079	-0.196	0.191
HSE06	0.887	-0.146	-0.061	-0.177	-0.063	-0.061	-0.057	-0.172	0.203

MPWB1K	-0.171	-0.112	-0.090	0.856	-0.125	-0.081	-0.082	0.175	0.211
M06-2X	-0.171	-0.112	-0.088	0.851	-0.133	-0.075	-0.079	-0.198	0.213
M08-HX	-0.170	-0.164	-0.086	0.536	0.065	-0.058	-0.057	0.603	0.217
MPW1B95	0.875	-0.155	-0.071	-0.099	-0.073	-0.069	-0.073	0.447	0.233
MPW1K	1.002	-0.173	-0.089	-0.204	-0.040	-0.081	-0.082	-0.199	0.234
MN15	-0.153	-0.156	-0.081	0.781	-0.159	-0.077	-0.082	0.416	0.238
MPW3LYP	0.782	-0.035	-0.045	0.669	-0.124	-0.049	-0.041	0.413	0.270
M11	1.009	-0.166	-0.085	0.772	-0.135	-0.039	-0.033	-0.194	0.304
M06-HF	1.046	-0.147	-0.113	0.885	0.067	-0.051	-0.081	-0.235	0.328
PWB6K	0.940	-0.171	-0.091	0.870	-0.033	-0.079	-0.080	0.665	0.366
Exptl. r_e	1.681	1.770	1.938	1.724	1.943	1.809	1.980	1.892	–

Table S3. The signed errors and mean unsigned errors (MUEs) for the calculated equilibrium bond dissociation energy ($D_e^{SP\text{-}ECP}$ in the units of kcal/mol) for various XC functionals, using the def2-QZVP basis combined with SDD ECP.

Functional	Cr_2	V_2	Mo_2	Rh_2	VNb	ScCo	YCo	NbCr	MUE
τ-HCTHhyb	2.1	0.1	8.4	5.0	-0.2	7.9	-11.0	-6.2	5.1
M05	-5.7	9.1	9.0	1.5	7.8	12.1	-12.5	-1.7	7.4
MN15	-9.0	13.0	-11.4	2.8	-2.0	12.6	-9.9	-13.6	9.3
M06-L	14.0	22.9	-6.9	9.3	10.5	23.6	-3.9	-4.8	12.0
BLYP	9.2	25.1	4.5	11.0	8.8	30.8	6.5	-2.3	12.3
N12-SX	-0.6	-24.3	3.3	-3.1	-14.5	-19.0	-32.8	-2.0	12.4
M06	-10.1	15.7	2.2	10.1	11.0	10.3	-14.4	-29.3	12.9
OreLYP	2.3	26.6	-1.4	10.3	10.3	39.0	12.7	-12.3	14.4
MN15-L	-14.0	1.8	-33.0	5.0	-14.1	20.6	-2.7	-24.4	14.5
RPBE	-6.4	31.7	-19.7	4.8	3.9	30.9	5.8	-15.3	14.8
OLYP	-2.0	28.2	-10.6	5.8	5.7	37.3	10.9	-18.8	14.9
O3LYP	-23.9	-0.8	-27.6	-10.1	-16.5	11.2	-11.2	-29.2	16.3
GAM	-4.9	18.1	-4.3	15.5	6.2	41.8	15.6	-25.2	16.4
revPBE	-7.2	33.8	-20.6	5.8	4.4	32.4	7.3	-21.9	16.7
B97-1	-15.6	-20.4	-8.0	-9.3	-18.0	-12.8	-28.2	-23.1	17.0
MOHLYP	-20.0	6.7	-33.6	-15.1	-15.5	13.8	-11.2	-38.5	19.3
TPSSh	-29.0	19.8	-34.5	-12.7	-10.0	4.6	-15.7	-33.1	19.9
N12	4.1	37.3	19.9	35.6	20.6	34.7	12.7	3.7	21.1
MPW3LYP	-30.0	-11.3	-29.0	-8.0	-23.2	-7.9	-25.3	-45.4	22.5
PBE	1.1	66.5	-9.8	15.4	25.6	43.0	17.3	-12.5	23.9
SOGGA11	-6.1	43.7	14.5	12.6	26.7	59.6	37.1	-7.6	26.0
M11-L	-9.5	-35.6	-15.3	-9.4	-31.5	-36.2	-59.5	-20.2	27.2
MGGA_MS2	-18.5	-38.0	-37.3	-15.9	-36.2	-13.6	-31.1	-28.7	27.4
B3LYP	-30.6	-22.6	-30.1	-18.4	-29.7	-13.7	-31.2	-45.7	27.7
PBEsol	11.8	61.6	1.4	27.8	28.1	61.0	33.5	2.3	28.4
SOGGA	9.2	63.1	-1.3	28.7	28.0	62.4	34.7	0.0	28.4
MGGA_MS0	-28.7	-7.0	-42.5	-22.3	-32.7	-27.1	-42.8	-32.4	29.5
MGGA_MS1	-26.9	-22.5	-42.3	-21.2	-39.2	-19.2	-36.1	-34.3	30.2
MN12-SX	14.6	-62.5	31.4	3.8	-18.8	-40.5	-53.1	17.6	30.3
B97-3	-32.2	-34.5	-25.2	-21.5	-32.3	-25.3	-40.5	-32.5	30.5
PW6B95	-42.1	-20.7	-39.3	-20.4	-32.9	-16.3	-31.7	-44.2	31.0
ωB97X	-25.8	-43.7	-21.6	-17.2	-36.0	-30.1	-43.9	-45.0	32.9
MPW1B95	-46.3	-22.1	-43.9	-21.8	-36.4	-19.7	-34.7	-48.8	34.2
ωB97X-D	-36.3	-38.0	-30.4	-18.5	-36.5	-24.7	-39.2	-55.5	34.9
M08-SO	-45.5	-22.0	-40.9	-13.0	-33.4	-32.8	-48.8	-47.9	35.5
HSE06	-47.2	-17.2	-49.8	-22.1	-37.2	-18.6	-35.5	-66.7	36.8
PBE0	-47.0	-17.3	-50.7	-22.9	-37.7	-18.8	-35.9	-67.2	37.2
B1LYP	-39.6	-40.5	-38.7	-26.0	-42.5	-29.9	-45.1	-43.0	38.2
MGGA_MS2h	-39.2	-34.8	-48.6	-23.3	-48.9	-30.0	-43.1	-44.7	39.1
M05-2X	-34.2	-51.3	-20.0	-19.7	-39.8	-51.7	-59.0	-58.9	41.8
M06-2X	-39.9	-57.7	-20.9	-32.6	-49.4	-45.6	-60.2	-40.4	43.3
MN12-L	23.5	-68.5	-12.1	-20.5	-46.7	-80.9	-90.4	7.8	43.8
MPWB1K	-61.5	-43.2	-61.0	-32.6	-55.0	-49.2	-59.4	-64.4	53.3
SOGGA11-X	-52.6	-64.1	-52.3	-27.1	-58.5	-59.1	-69.8	-55.4	54.9
M11	-72.9	-37.2	-64.6	-35.3	-52.3	-40.0	-48.9	-101.8	56.6
M08-HX	-58.8	-56.7	-47.0	-28.6	-56.5	-58.4	-68.5	-82.0	57.1
PWB6K	-63.3	-49.5	-63.1	-34.3	-59.0	-56.1	-65.0	-66.1	57.1
τ-HCTH	38.8	45.2	41.5	110.8	40.0	102.1	72.5	34.8	60.7
M06-HF	-55.3	-129.4	-18.7	-48.3	-73.8	-48.9	-52.9	-86.0	64.2
MPW1K	-69.5	-47.6	-75.9	-39.8	-70.4	-53.6	-64.3	-98.5	65.0
Exptl. D_e	36.0	64.2	103.9	55.9	88.1	56.8	60.0	70.3	–

Table S4. The signed errors and mean unsigned errors (MUEs) for the calculated equilibrium bond dissociation energy ($D_e^{SP\text{-}DKH}$ in the units of kcal/mol) for various XC functionals, using aug-cc-pwCVTZ-DK all-electron basis and DKH2.

Functional	Cr_2	V_2	Mo_2	Rh_2	VNb	ScCo	YCo	NbCr	MUE
τ-HCTHhyb	0.2	-4.9	4.0	10.8	-0.3	4.6	-5.0	1.6	3.9
M06-L	-3.3	-8.0	-16.9	-7.2	-8.8	9.9	-4.6	-5.6	8.0
N12-SX	11.8	-14.1	5.7	-0.9	-6.1	-11.3	-17.8	-2.1	8.7
OreLYP	0.3	16.3	-1.7	10.5	7.3	24.8	13.0	-1.1	9.4
GAM	-7.6	4.6	-19.4	12.5	-4.4	20.6	6.3	-10.8	10.8
OLYP	-5.6	17.1	-11.3	6.4	2.3	23.9	11.6	-16.1	11.8
MN12-L	21.6	-16.7	-6.8	-16.9	-17.8	-4.2	-13.3	1.7	12.4
RPBE	-6.4	23.5	-21.5	5.9	1.7	22.7	10.7	-17.3	13.7
M05	-16.7	-19.5	-10.7	-6.3	-12.8	-11.0	-23.1	-11.9	14.0
BLYP	14.4	25.1	5.5	13.1	11.4	26.9	13.0	7.1	14.6
revPBE	-7.4	26.1	-22.1	6.9	2.6	24.8	12.6	-18.1	15.1
TPSSh	-25.5	-5.0	-32.0	-9.1	-17.9	-1.8	-10.3	-26.3	16.0
O3LYP	-29.3	-12.3	-28.6	-9.1	-20.1	-1.5	-10.9	-28.7	17.6
M06	-26.3	-23.5	-9.3	-10.6	-13.4	-14.0	-25.6	-18.8	17.7
PBE	2.7	37.3	-10.7	16.5	13.2	35.4	22.4	-3.6	17.7
B97-1	-18.8	-27.0	-10.1	-4.5	-18.5	-22.1	-27.8	-14.7	17.9
MGGA_MS2	-19.9	-18.3	-26.7	-12.0	-25.5	-6.4	-12.9	-21.3	17.9
MOHLYP	-26.4	-6.7	-36.1	-14.0	-20.6	0.9	-10.2	-29.6	18.1
M11-L	7.3	-20.9	-23.0	-31.5	-21.8	-27.1	-41.0	-1.7	21.8
MN15-L	-27.2	-24.1	-38.4	-9.2	-27.7	-5.5	-13.7	-30.0	22.0
MGGA_MS1	-27.9	-22.3	-32.2	-15.0	-29.4	-11.9	-17.9	-28.4	23.1
MN12-SX	20.0	-44.0	13.2	-13.4	-15.2	-31.7	-36.5	17.9	24.0
MGGA_MS0	-27.6	-26.5	-31.1	-15.8	-31.3	-16.3	-21.7	-26.2	24.6
SOGGA11	10.0	59.2	17.6	-7.8	38.5	32.4	28.3	15.0	26.1
MN15	-29.8	-28.7	-34.7	-14.8	-32.2	-13.1	-18.6	-38.4	26.3
SOGGA	9.0	53.8	-0.8	29.1	25.8	51.2	37.6	3.3	26.3
PBEsol	11.9	53.1	1.9	28.5	26.4	50.8	36.8	5.7	26.9
B3LYP	-32.9	-29.6	-30.4	-16.8	-30.4	-23.0	-30.8	-31.7	28.2
MPW3LYP	-32.6	-34.0	-29.3	-17.1	-31.8	-14.2	-21.4	-47.2	28.4
N12	12.2	52.0	16.7	25.6	28.0	50.4	35.3	9.9	28.8
B97-3	-35.7	-47.1	-24.5	-20.4	-35.4	-43.7	-47.3	-30.1	35.5
PW6B95	-46.5	-38.2	-41.3	-18.5	-37.8	-27.4	-31.8	-42.3	35.5
ωB97X	-26.8	-50.7	-28.0	-18.1	-39.6	-38.8	-44.9	-40.6	35.9
B97X-D	-39.8	-43.7	-33.3	-18.5	-38.3	-36.6	-42.2	-36.1	36.1
τ-HCTH	40.8	31.4	37.2	33.2	33.5	45.9	30.3	37.2	36.2
HSE06	-51.6	-33.3	-52.3	-21.3	-41.3	-26.0	-31.9	-49.4	38.4
PBE0	-52.6	-34.4	-52.5	-21.6	-42.1	-26.8	-32.3	-50.1	39.0
MGGA_MS2h	-37.4	-53.7	-40.2	-24.9	-40.8	-29.4	-33.9	-55.3	39.4
B1LYP	-42.8	-48.3	-39.1	-25.0	-43.7	-42.6	-48.5	-40.8	41.3
MPW1B95	-52.5	-43.0	-45.9	-20.2	-42.4	-31.8	-35.4	-64.0	41.9
M05-2X	-37.9	-81.9	-25.1	-13.1	-53.8	-71.9	-68.1	-51.0	50.4
M11	-70.3	-37.5	-71.5	-17.8	-49.1	-50.0	-49.4	-86.2	54.0
SOGGA11-X	-56.0	-78.7	-52.7	-27.0	-62.6	-55.1	-56.9	-52.6	55.2
M06-2X	-45.7	-87.7	-29.6	-34.1	-59.3	-102.1	-100.3	-58.3	64.6
PWB6K	-71.3	-76.3	-65.5	3.1	-71.0	-83.3	-82.1	-66.1	64.8
MPWB1K	-69.9	-70.5	-63.3	-32.2	-66.9	-75.7	-75.2	-87.4	67.6
M08-HX	-70.2	-82.7	-67.2	-26.7	-69.0	-72.6	-75.6	-89.3	69.2
MPW1K	-78.6	-70.3	-77.6	-39.6	-76.6	-82.1	-76.4	-54.4	69.5
M08-SO	-70.1	-77.8	-71.3	-26.4	-71.2	-77.7	-76.1	-91.2	70.2
M06-HF	-52.2	-113.1	-31.7	-44.8	-81.4	-104.2	-82.2	-57.6	70.9
Exptl. D_e	36.0	64.2	103.9	55.9	88.1	56.8	60.0	70.3	–

Table S5. The signed errors and mean unsigned errors (MUEs) for the calculated equilibrium bond dissociation energy ($D_e^{opt\text{-}ECP}$ in the units of kcal/mol) for various XC functionals, using the def2-QZVP basis combined with SDD ECP.

Functional	Cr_2	V_2	Mo_2	Rh_2	VNb	ScCo	YCo	NbCr	MUE
τ-HCTHhyb	-11.1	-7.7	7.0	5.1	0.5	9.5	-10.3	-1.9	6.7
M05	-20.4	12.6	8.6	2.9	10.6	14.0	-11.9	-1.7	10.3
M06-L	6.4	25.0	-7.8	9.3	11.3	24.6	-3.6	5.9	11.7
BLYP	5.1	25.9	4.5	11.0	9.0	31.0	6.5	1.1	11.8
MN15	-20.0	21.0	-14.6	1.7	-0.2	16.2	-8.6	-13.2	11.9
M06	-25.6	18.6	1.7	10.8	12.2	12.4	-13.5	-8.5	12.9
N12-SX	-13.7	-24.8	1.5	-3.0	-14.7	-17.4	-32.0	-4.2	13.9
OreLYP	-5.0	29.0	-1.9	10.3	11.4	40.2	13.0	-3.5	14.3
OLYP	-8.6	30.7	-11.4	5.9	6.9	38.4	11.3	-10.2	15.4
RPBE	-12.0	33.0	-20.3	4.8	4.3	31.3	5.8	-16.2	16.0
GAM	-18.4	21.0	-6.6	15.6	7.3	42.8	15.8	-6.0	16.7
revPBE	-12.8	35.1	-21.2	5.8	4.9	32.9	7.3	-17.1	17.1
MN15-L	-30.0	5.8	-37.4	5.5	-12.0	22.3	-1.7	-23.5	17.3
B97-1	-32.2	-20.2	-10.0	-9.8	-17.9	-11.2	-27.6	-20.0	18.6
O3LYP	-38.4	2.7	-29.9	-10.2	-14.4	13.3	-10.4	-32.9	19.0
MOHLYP	-27.8	8.4	-35.1	-14.9	-14.7	14.4	-11.1	-30.4	19.6
N12	1.7	39.9	20.7	35.7	21.7	36.1	13.2	4.9	21.8
TPSSh	-43.9	21.5	-36.8	-12.8	-9.5	5.7	-15.3	-36.5	22.8
PBE	-3.8	68.1	-10.1	15.4	26.2	43.7	17.5	-7.3	24.0
MPW3LYP	-48.9	-21.2	-31.4	-8.3	-22.9	-6.3	-24.7	-37.3	25.1
MGGA_MS2	-23.7	-18.5	-38.7	-17.0	-36.6	-13.0	-31.0	-28.7	25.9
SOGGA11	-11.2	45.1	14.5	12.1	27.5	60.0	37.1	0.9	26.1
SOGGA	5.1	65.6	-1.3	29.1	29.1	64.0	35.3	0.2	28.7
PBEsol	8.0	64.0	1.5	28.1	29.2	62.4	34.0	2.6	28.7
MN12-SX	-5.3	-69.2	29.7	1.8	-19.5	-40.1	-52.9	13.4	29.0
B3LYP	-48.1	-25.5	-32.0	-18.6	-29.5	-12.3	-30.7	-38.0	29.4
MGGA_MS0	-28.7	-9.9	-44.6	-19.3	-33.3	-26.4	-42.7	-32.3	29.7
MGGA_MS1	-32.4	-22.3	-44.3	-19.1	-39.7	-18.4	-35.9	-34.2	30.8
M11-L	-26.8	-36.3	-16.4	-9.6	-31.6	-45.0	-62.7	-18.5	30.9
PW6B95	-50.6	-20.2	-42.6	-21.0	-32.1	-16.5	-30.7	-46.3	32.5
B97-3	-55.4	-33.8	-28.7	-19.1	-31.8	-23.1	-39.5	-37.8	33.7
ωB97X	-51.5	-46.9	-26.0	-13.3	-35.2	-27.2	-42.5	-48.2	36.4
ωB97X-D	-59.6	-37.1	-33.3	-16.3	-35.7	-22.2	-38.0	-55.8	37.3
HSE06	-71.4	-20.8	-54.0	-21.8	-37.3	-16.4	-34.5	-43.3	37.4
MPW1B95	-73.5	-21.6	-47.8	-22.5	-35.3	-16.7	-33.3	-51.3	37.8
PBE0	-71.7	-20.6	-55.2	-23.7	-36.7	-16.3	-34.6	-56.9	39.5
M08-SO	-74.2	-23.8	-46.4	-14.6	-34.5	-31.0	-47.8	-54.9	40.9
MGGA_MS2h	-48.6	-38.1	-51.5	-25.6	-49.2	-28.9	-44.9	-44.7	41.4
B1LYP	-61.8	-44.0	-41.7	-26.7	-43.2	-28.4	-44.5	-43.8	41.8
MN12-L	16.4	-66.1	-13.6	-23.0	-47.0	-80.9	-90.4	8.6	43.2
M05-2X	-80.5	-62.9	-27.5	-25.5	-49.5	-47.2	-56.8	-49.9	50.0
M06-2X	-86.5	-71.5	-28.5	-35.9	-48.7	-46.1	-61.7	-56.1	54.4
MPWB1K	-75.4	-55.2	-67.9	-37.1	-55.0	-46.8	-57.3	-66.7	57.7
SOGGA11-X	-90.8	-58.0	-58.2	-20.5	-57.8	-56.0	-68.0	-68.2	59.7
τ-HCTH	31.1	48.4	40.4	111.0	41.7	101.6	70.8	34.8	60.0
PWB6K	-107.5	-56.0	-70.5	-25.9	-59.0	-53.7	-63.0	-46.7	60.3
M11	-110.6	-56.7	-72.6	-41.7	-54.5	-37.8	-48.0	-80.6	62.8
M08-HX	-104.3	-73.6	-54.0	-24.1	-63.2	-55.7	-65.7	-72.7	64.2
MPW1K	-113.6	-62.4	-84.9	-45.4	-63.7	-50.1	-62.2	-89.9	71.5
M06-HF	-145.8	-132.4	-31.9	-69.6	-71.8	-64.5	-69.3	-19.6	75.6
Exptl. D_e	36.0	64.2	103.9	55.9	88.1	56.8	60.0	70.3	–

Table S6. The signed errors and mean unsigned errors (MUEs) for the calculated equilibrium bond dissociation energy ($D_e^{\text{opt-DKH}}$ in the units of kcal/mol) for various XC functionals, using aug-cc-pwCVTZ-DK all-electron basis and DKH2.

Functional	Cr_2	V_2	Mo_2	Rh_2	VNb	ScCo	YCo	NbCr	MUE
τ-HCTHhyb	10.4	-3.1	2.4	10.9	0.2	5.5	-4.4	-21.5	7.3
N12-SX	10.9	-14.4	4.2	-1.4	-9.5	-10.5	-17.3	2.3	8.8
M06-L	-14.3	-7.2	-18.9	-9.2	-8.4	10.3	-4.4	-4.1	9.6
OreLYP	1.4	17.3	-2.0	10.5	8.0	25.2	13.3	-1.1	9.8
OLYP	-4.8	18.1	-11.9	6.4	3.0	24.3	11.8	-16.1	12.0
MN12-L	21.7	-17.5	-8.8	-16.1	-22.2	-3.1	-12.6	3.2	13.2
RPBE	-10.3	23.8	-22.1	5.9	1.8	22.8	10.7	-17.8	14.4
BLYP	14.4	25.2	5.5	13.2	11.4	27.0	13.0	7.1	14.6
GAM	-20.5	5.9	-22.8	12.2	-3.7	20.9	6.5	-26.9	14.9
M05	-33.8	-16.8	-13.2	-6.3	-10.8	-10.6	-22.7	-11.2	15.7
revPBE	-11.1	26.4	-22.6	6.9	2.8	24.8	12.6	-18.6	15.7
B97-1	1.1	-26.4	-12.1	-4.7	-21.3	-21.3	-27.2	-16.7	16.4
MGGA_MS2	-10.2	-18.3	-27.8	-11.8	-27.0	-6.2	-12.6	-21.9	17.0
PBE	0.0	37.8	-11.0	16.5	13.4	35.6	22.5	-3.6	17.6
MN15-L	0.5	-21.1	-43.1	-9.3	-25.4	-4.1	-12.3	-27.6	17.9
TPSSh	-10.4	-10.7	-34.1	-9.3	-44.1	-1.3	-9.9	-28.9	18.6
MOHLYP	-33.5	-6.3	-37.6	-13.7	-20.3	0.9	-10.2	-37.6	20.0
M06	-44.5	-22.8	-11.2	-14.7	-12.1	-13.3	-25.2	-18.4	20.3
O3LYP	-42.1	-10.1	-31.0	-9.3	-20.2	-0.5	-10.2	-50.2	21.7
MN12-SX	4.0	-43.9	10.2	-16.1	-22.2	-30.8	-35.8	18.1	22.6
MPW3LYP	-8.0	-33.6	-31.6	-17.5	-35.0	-13.5	-20.9	-30.4	23.8
M11-L	7.3	-21.9	-28.6	-34.3	-29.1	-25.7	-39.9	-10.3	24.6
MGGA_MS0	-30.7	-32.1	-32.8	-16.9	-34.1	-16.0	-21.3	-26.2	26.3
MGGA_MS1	-34.1	-28.7	-33.9	-15.8	-31.1	-11.6	-17.5	-37.7	26.3
SOGGA	7.3	54.9	-0.7	29.5	26.6	52.0	38.1	3.6	26.6
PBEsol	10.5	54.1	2.1	28.8	27.1	51.5	37.2	5.8	27.1
MN15	-49.1	-25.1	-39.7	-15.9	-32.2	-11.2	-16.7	-30.0	27.5
SOGGA11	10.1	59.0	17.5	-35.5	38.0	32.4	28.3	15.0	29.5
N12	15.7	53.5	17.9	25.7	29.0	51.3	35.8	11.7	30.1
B3LYP	-47.4	-33.0	-32.4	-16.9	-33.6	-22.4	-30.4	-32.5	31.1
MPW1B95	-16.0	-48.1	-50.0	-20.9	-43.0	-30.3	-34.2	-41.3	35.5
ωB97X	0.4	-53.0	-29.7	-15.2	-42.8	-37.2	-43.7	-62.3	35.5
τ-HCTH	34.2	33.4	36.1	33.3	34.8	46.9	30.8	37.2	35.8
PW6B95	-67.3	-37.6	-44.8	-19.4	-38.7	-26.3	-30.9	-37.8	37.8
ωB97X-D	-29.0	-45.8	-36.6	-17.2	-39.2	-35.3	-41.1	-65.8	38.7
HSE06	-16.2	-37.5	-56.6	-21.6	-41.6	-24.9	-31.0	-84.5	39.2
B97-3	-56.3	-47.3	-27.9	-18.2	-36.5	-42.6	-46.4	-47.4	40.3
B1LYP	-11.2	-48.1	-42.0	-25.0	-45.3	-41.9	-48.0	-75.5	42.1
MGGA_MS2h	-49.2	-44.5	-42.8	-21.0	-45.6	-28.8	-33.3	-92.0	44.6
PBE0	-74.3	-38.7	-57.1	-22.7	-45.8	-25.5	-31.2	-69.5	45.6
M11	-21.1	-49.2	-79.6	-19.9	-56.7	-50.1	-49.0	-109.0	54.3
PWB6K	-17.4	-91.6	-73.2	-1.3	-81.0	-81.4	-80.4	-77.2	62.9
M05-2X	-81.2	-87.9	-32.7	-14.4	-60.2	-68.0	-62.6	-96.9	63.0
SOGGA11-X	-89.5	-86.6	-58.5	-21.0	-67.7	-53.4	-55.4	-77.2	63.7
M08-HX	-113.0	-95.4	-76.1	-28.5	-76.9	-79.5	-74.8	-38.0	72.8
MPWB1K	-108.2	-95.9	-70.5	-35.8	-72.9	-73.7	-73.4	-54.6	73.1
MPW1K	-20.2	-85.0	-86.8	-44.5	-77.3	-80.1	-80.6	-112.3	73.3
M06-2X	-88.5	-91.9	-38.0	-36.5	-67.0	-97.8	-94.6	-103.7	77.2
M08-SO	-114.1	-90.3	-79.5	-28.3	-74.4	-77.2	-78.5	-104.0	80.8
M06-HF	22.3	-140.1	-45.7	-53.4	-75.5	-112.4	-94.4	-138.0	85.2
Exptl. D_e	36.0	64.2	103.9	55.9	88.1	56.8	60.0	70.3	–