FHI-aims benchmark for BEEFvdW, vdW-DF2 and mBEEFvdW

Svenja M. Janke[1], Reinhard J. Maurer[1,2], Andrew J. Logsdail[3]

[1] Department of Chemistry, University of Warwick, Coventry, UK
[2] Department of Physics, University of Warwick, Coventry, UK
[3] School of Chemistry, University of Cardiff, Cardiff, UK

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1 General

The FHI-aims benchmark for BEEFvdW, vdW-DF2 and mBEEFvdW were done using 'tight' settings on Archer (128 cores, Intel E5-2680v4 (Broadwell)), Athena (28 cores, Intel E5-2680v4 (Broadwell)) and Orac (28 cores, Intel Xeon Phi 7250F (Knights Landing)) using the S22 benchmark set [1] in early 2021. The benchmark data is available at DOI: 10.17172/NOMAD/2023.09.25-1

To compare the benchmark calculations to the original data from Wellendorff *et al.* [4], Lee *et al.* [2] and Lundgaard *et al.* [3], the following comparisons are used, where $N = 22$, the number of tests, x_i^{ref} is the value against which we benchmark, x_i^{calc} is the newly calculated value:

$$MSD = \frac{1}{N}\sum_i x_i^{\text{ref}} - x_i^{\text{calc}} \tag{1}$$

$$MAD = \frac{1}{N}\sum_i |x_i^{\text{ref}} - x_i^{\text{calc}}| \tag{2}$$

$$SD = \sqrt{\frac{1}{N}\sum_i (x_i^{\text{ref}} - x_i^{\text{calc}})^2} \tag{3}$$

Table 1: S22 Benchmark set summary for different functionals and different errors, including maximum deviation. Reference data from [2–4]. The largest deviations are for [1]: Adenine-Thymine [2] Benzene dimer T-shpae, [3] Adenine-Thymine (stacked) [4] Indol-benzene (stacked), [5] Uracil dimer (stacked).

Error	beef-vdw vs[4] (eV)	beef2-vdw2 vs [4] (eV)	vdw-df2 vs [2]	mbeef2_vdw2 vs [3] (eV)
MSD	0.012	-0.012	-0.022	0.038
MAD	0.013	0.013	0.022	0.038
STD	0.018	0.018	0.029	0.046
max.	0.042[1]	0.041[2]	0.062[3,4]	0.115[5]

2 Summary of BEEFvdW benchmark

We performed the benchmark for using BEEF-vdW with FHI-aims on Athena. In principle, there are two possible ways to use BEEF-vdW in FHI-aims, 'beef-vdw' and 'beef2-vdw2'. Both of them make use of libxc, 'beef-vdw' uses both exchange and correlation from libxc, 'beef2-vdw2' uses only the exchange from libxc and 'canonical local correlation' according to the FHI-aims code comments. Take note that both are relatively slow (i.e., calculations of molecules at metal surfaces does not appear possible).

Table 2: S22 Benchmark set, FHI-aims's 'xc beef-vdw' total energies obtained with BEEFvdW with the Libxc implementation of both exchange and correlation and the binding energy E_{bind} of the molecular systems, compared to values form the original BEEFvdW paper of Wellendorff et al. [4]. Calculations were performed on Athena with 28 cores.

System	mol 1 (eV)	mol 2(eV)	total (eV)	E_{bind} (eV)	E_{bind} (eV)[4]	time (s)
2pyridoxine_2aminopyridine	-8861.8584967	-8318.3525724	-17180.8424101	-0.631	-0.62	18672
adenine_thymine_stack	-12799.1613247	-12438.1724084	-25237.6343443	-0.301	-0.303	41988
adenine_thymine_wc	-12799.1613247	-12438.1724084	-25237.9660554	-0.632	-0.59	30225
ammonia_dimer	-1549.5676088	-1549.5676088	-3099.2535610	-0.118	-0.116	1715
benzene_ammonia	-6363.9121251	-1549.5676088	-7913.5633200	-0.084	-0.083	9686
benzene_dimer_stack	-6363.9121251	-6363.912125	-12727.9203951	-0.096	-0.077	21634
benzene_dimer2_Tshape	-6363.9121251	-6363.9121251	-12727.9093941	-0.085	-0.053	16731
benzene_hcn	-6363.9121251	-2558.8645256	-8922.9287316	-0.152	-0.15	9253
benzene_methane	-6363.9121251	-1111.1685336	-7475.1307144	-0.050	-0.05	8718
benzene_water	-6363.9121251	-2093.0140681	-8457.0568949	-0.131	-0.118	8125
ethene_ethine	-2154.1088494	-2119.0859824	-4273.2653662	-0.071	-0.07	3163
ethene_dimer	-2154.1088494	-2154.1088494	-4308.2934795	-0.076	-0.06	3862
formamide_dimer	-4653.0000572	-4653.0000572	-9306.5790317	-0.579	-0.57	5901
formic_acid_dimer	-5196.3397819	-5196.3397819	-10393.3762467	-0.697	-0.676	5224
indol_benzene_stack	-9967.5837516	-6363.9121251	-16331.5715230	-0.076	-0.079	32963
indole_benzene_tshape	-9967.5837516	-6363.9121251	-16331.6900074	-0.194	-0.171	24252
methane_dimer	-1111.1685336	-1111.1685336	-2222.3750592	-0.038	-0.041	1941
phenol_dimer	-8423.2063472	-8423.2063472	-16846.6666973	-0.254	-0.214	21675
pyrazin_dimer	-7240.1918285	-7240.1918285	-14480.4755616	-0.092	-0.099	18862
uracil_dimer	-11360.5115167	-11360.5115167	-22721.3500095	-0.327	-0.315	32699
uracil_dimer(stack)	-11360.5115167	-11360.5115167	-22721.7889874	-0.766	-0.747	21237
water_dimer	-2093.0140681	-2093.0140681	-4186.2221855	-0.194	-0.186	1191

Table 3: S22 Benchmark set, FHI-aims's 'xc beef2-vdw2' total energies obtained with BEEFvdW using libxc exchange and 'canonical local correlation' within FHI-aims and the binding energy E_{bind} of the molecular systems, compared to values from the original BEEFvdW paper of Wellendorff et al. [4]. Calculations were performed on Athena with 28 cores.

System	mol 1 (eV)	mol 2(eV)	total (eV)	E_{bind} (eV)	E_{bind} (eV)[4]	time(s)
2pyridoxine_2aminopyridine	-8861.5611883	-8318.0740372	-17180.2679924	-0.633	-0.62	17858
adenine_thymine_stack	-12798.9084111	-12437.8806626	-25237.0935724	-0.304	-0.303	42909
adenine_thymine_wc	-12798.9084111	-12437.8806626	-25237.4122473	-0.623	-0.59	29431
ammonia_dimer	-1549.5732269	-1549.5732269	-3099.2643926	-0.118	-0.116	1638
benzene_ammonia	-6363.5646397	-1549.5732269	-7913.2207882	-0.083	-0.083	9870
benzene_dimer_stack	-6363.5646397	-6363.5646397	-12727.1989487	-0.070	-0.077	20617
benzene_dimer2_Tshape	-6363.5646397	-6363.5646397	-12727.2232525	-0.094	-0.053	17550
benzene_hcn	-6363.5646397	-2558.8123852	-8922.5344310	-0.157	-0.15	9261
benzene_methane	-6363.5646397	-1111.1123991	-7474.7310344	-0.054	-0.05	9418
benzene_water	-6363.5646397	-2093.0008028	-8456.6961494	-0.131	-0.118	8293
ethene_ethine	-2153.9947773	-2118.9701291	-4273.0365330	-0.072	-0.07	3267
ethene_dimer	-2153.9947773	-2153.9947773	-4308.0591633	-0.070	-0.06	3929
formamide_dimer	-4652.9333628	-4652.9333628	-9306.4450091	-0.578	-0.57	5955
formic_acid_dimer	-5196.2593235	-5196.2593235	-10393.2156826	-0.697	-0.676	4955
indol_benzene_stack	-9967.1238084	-6363.5646397	-16330.7682477	-0.080	-0.079	33334
indole_benzene_tshape	-9967.1238084	-6363.5646397	-16330.8917031	-0.203	-0.171	25796
methane_dimer	-1111.1123991	-1111.1123991	-2222.2647464	-0.040	-0.041	2044
phenol_dimer	-8422.8502982	-8422.8502982	-16845.9540681	-0.253	-0.214	20268
pyrazin_dimer	-7239.9784544	-7239.9784544	-14480.0489132	-0.092	-0.099	19359
uracil_dimer	-11360.2697195	-11360.2697195	-22720.8748158	-0.335	-0.315	32611
uracil_dimer(stack)	-11360.2697195	-11360.2697195	-22721.3060601	-0.767	-0.747	21093
water_dimer	-2093.0008028	-2093.0008028	-4186.1964032	-0.195	-0.186	1218

3 Summary of vdW-DF benchmark

Table 4: S22 Benchmark set, FHI-aims's 'xc vdw-df2' total energies obtained with vdW-DF2 within FHI-aims and the binding energy E_{bind} of the molecular systems, compared to values from [2]. Calculations were performed on Orac with 28 cores.

System	mol 1 (eV)	mol 2(eV)	total (eV)	E_{bind} (eV)	E_{bind} (eV)[2]	time(s)
2pyridoxine 2aminopyridine	-8866.9566271	-8323.7022138	-17191.3321702	-0.673	-0.687	18351.55
adenine thymine stack	-12806.6075487	-12444.7609566	-25251.7727979	-0.404	-0.466	38900.26
adenine thymine wc	-12806.6075487	-12444.7609566	-25252.0033221	-0.635	-0.66	27782.64
ammonia dimer	-1550.7270869	-1550.7270869	-3101.5854440	-0.131	-0.134	1629.58
benzene ammonia	-6368.3196083	-1550.7270869	-7919.1301017	-0.083	-0.092	8852.83
benzene dimer stack	-6368.3196083	-6368.3196083	-12736.7213648	-0.082	-0.123	20089.47
benzene dimer2 Tshape	-6368.3196083	-6368.3196083	-12736.7274432	-0.088	-0.105	16436.88
benzene hcn	-6368.3196083	-2560.6684174	-8929.1425704	-0.155	-0.17	9385.52
benzene methane	-6368.3196083	-1112.2690065	-7480.6409374	-0.052	-0.063	9338.83
benzene water	-6368.3196083	-2093.9097863	-8462.3550328	-0.126	-0.129	8862.81
ethene ethine	-2155.9229194	-2120.7986626	-4276.7875323	-0.066	-0.07	3085.83
ethene dimer	-2155.9229194	-2155.9229194	-4311.9025959	-0.057	-0.065	3852.44
formamide dimer	-4655.4712026	-4655.4712026	-9311.5734293	-0.631	-0.655	5921.18
formic acid dimer	-5198.5627720	-5198.5627720	-10397.8584236	-0.733	-0.766	5065.87
indol benzene stack	-9973.8988733	-6368.3196083	-16342.3530636	-0.135	-0.197	32245.87
indole benzene tshape	-9973.8988733	-6368.3196083	-16342.4058076	-0.187	-0.206	23377.00
methane dimer	-1112.2690065	-1112.2690065	-2224.5685036	-0.030	-0.03	1923.48
phenol dimer	-8428.2503677	-8428.2503677	-16856.7569490	-0.256	-0.279	21757.28
pyrazin dimer	-7244.7879304	-7244.7879304	-14489.7138567	-0.138	-0.177	18950.99
uracil dimer	-11366.2841466	-11366.2841466	-22733.3833275	-0.815	-0.832	20424.85
uracil dimer1 stack	-11366.2841466	-11366.2841466	-22732.9790344	-0.411	-0.402	31560.85
water dimer	-2093.9097863	-2093.9097863	-4188.0369039	-0.217	-0.218	1180.71

4 Benchmark mBEEF-vdW

The calculations for the mBEEF-vdW with 'tight' show some surprisingly high deviations between the reference data [3] and the FHI-aims calculated data, particularly for the uracil stacked dimer case of 115 meV. We looked at the basis set (light, and really-tight for the largest deviating cases) to see if the deviation is a matter of convergence, which it does not appear to be the case.

Table 5: S22 Benchmark set, FHI-aims's 'xc mbeef2_vdw2' total energies obtained with mBEEFvdW and 'tight' settings within FHI-aims and the binding energy E_{bind} of the molecular systems, compared to values from [2]. Calculations were performed on Orac with 28 cores.

System	mol 1 (eV)	mol 2(eV)	total (eV)	E_{bind} (eV)	E_{bind} (eV)[3]	time(s)
2pyridoxine 2aminopyriding	-8814.3701284	-8272.2566949	-17087.3912665	-0.764	-0.706	22854.95
adenine thymine stack	-12732.1045083	-12374.4737891	-25107.1814889	-0.603	-0.539	46855.10
adenine thymine wc	-12732.1045083	-12374.4737891	-25107.3016758	-0.723	-0.671	33759.71
ammonia dimer	-1541.1072563	-1541.1072563	-3082.3532419	-0.138	-0.127	1870.90
benzene ammonia	-6326.2000181	-1541.1072563	-7867.4276032	-0.120	-0.109	9711.13
benzene dimer stack	-6326.2000181	-6326.2000181	-12652.5564432	-0.156	-0.135	20381.13
benzene dimer2 Tshape	-6326.2000181	-6326.2000181	-12652.5345340	-0.134	-0.108	16936.68
benzene hcn	-6326.2000181	-2544.9434218	-8871.3648428	-0.221	-0.196	10331.68
benzene methane	-6326.2000181	-1103.6156339	-7429.8917084	-0.076	-0.067	9604.01
benzene water	-6326.2000181	-2083.2057605	-8409.5820563	-0.176	-0.151	9098.88
ethene ethine	-2140.5577508	-2106.1232572	-4246.7636805	-0.083	-0.068	3525.49
ethene dimer	-2140.5577508	-2140.5577508	-4281.1891447	-0.074	-0.056	4261.47
formamide dimer	-4629.6927944	-4629.6927944	-9260.1130154	-0.727	-0.670	7219.79
formic acid dimer	-5171.6946343	-5171.6946343	-10344.2951530	-0.906	-0.830	5300.43
indol benzene stack	-9910.7252692	-6326.2000181	-16237.1661224	-0.241	-0.212	32215.50
indole benzene tshape	-9910.7252692	-6326.2000181	-16237.1801750	-0.255	-0.221	25928.87
methane dimer	-1103.6156339	-1103.6156339	-2207.2617795	-0.031	-0.030	2162.41
phenol dimer	-8376.7237704	-8376.7237704	-16753.7690469	-0.322	-0.272	24691.62
pyrazin dimer	-7200.5894088	-7200.5894088	-14401.4075462	-0.229	-0.199	22286.31
uracil dimer	-11303.3475053	-11303.3475053	-22607.6225781	-0.928	-0.856	23332.18
uracil dimer1 stack	-11303.3475053	-11303.3475053	-22607.2664421	-0.571	-0.456	34259.85
water dimer	-2083.2057605	-2083.2057605	-4166.6541873	-0.243	-0.209	1514.96

Table 6: S22 Benchmark set, FHI-aims's 'xc mbeef2_vdw2' total energies obtained with mBEEFvdW and 'light' settings within FHI-aims and the binding energy E_{bind} of the molecular systems, compared to values from [2]. Calculations were performed on Athena (*, 28 cores), Archer (128 cores) and Orac (†, 28 cores).

System	mol 1 (eV)	mol 2(eV)	total (eV)	E_{bind} (eV)	E_{bind} (eV)[3]	time(s)
2pyridoxine 2aminopyriding	-8813.3634410	-8271.2578170	-17085.3912069	-0.770	-0.706	7133.93
adenine thymine stack*	-12730.4338372	-12373.0402066	-25107.1814889	-0.603	-0.539	12462.07
adenine thymine wc	-12730.4338372	-12373.0402066	-25104.1943908	-0.720	-0.671	10914.56
ammonia dimer	-1540.9495780	-1540.9495780	-3082.0439670	-0.138	-0.127	653.58
benzene ammonia	-6325.5056667	-1540.9495780	-7866.5738635	-0.119	-0.109	3669.18
benzene dimer stack	-6325.5056667	-6325.5056667	-12651.1681708	-0.157	-0.135	8090.48
benzene dimer2 Tshape	-6325.5056667	-6325.5056667	-12651.1445275	-0.133	-0.108	6186.39
benzene hcn†	-6325.5056667	-2544.6688105	-8870.3908219	-0.216	-0.196	2826.28
benzene methane	-6325.5056667	-1103.5249079	-7429.1066571	-0.076	-0.067	3803.43
benzene water	-6325.5056667	-2083.0398582	-8408.7163446	-0.171	-0.151	3513.31
ethene dimer	-2140.3559824	-2140.3559824	-4280.7838505	-0.072	-0.056	1584.93
ethene ethine	-2140.3559824	-2105.8945800	-4246.3286045	-0.078	-0.068	1184.234
formamide dimer	-4629.2086939	-4629.2086939	-9259.1379999	-0.721	-0.670	2548.62
formic acid dimer*	-5171.2184714	-5171.2184714	-10343.3098107	-0.873	-0.830	1834.81
indol benzene stack	-9909.5203877	-6325.5056667	-16235.2730335	-0.247	-0.212	11382.65
indole benzene tshape	-9909.5203877	-6325.5056667	-16235.2785222	-0.252	-0.221	8673.20
methane dimer	-1103.5249079	-1103.5249079	-2207.0811480	-0.031	-0.030	818.27
phenol dimer	-8375.8040019	-8375.8040019	-16751.9330146	-0.325	-0.272	7465.98
pyrazin dimer	-7199.6975663	-7199.6975663	-14399.6320560	-0.237	-0.199	7618.10
uracil dimer*	-11302.0277733	-11302.0277733	-22604.9705554	-0.915	-0.856	6214.65
uracil dimer1 stack*	-11302.0277733	-11302.0277733	-22604.6161700	-0.561	-0.456	9658.46
water dimer	-2083.0398582	-2083.0398582	-4166.3263700	-0.247	-0.209	575.81

Table 7: Selected geometries from the S22 Benchmark set, FHI-aims's 'xc mbeef2_vdw2' total energies obtained with mBEEFvdW and 'really_tight' settings within FHI-aims and the binding energy E_{bind} of the molecular systems, compared to values from [2]. The selected geometries are the ones that showed the highest deviations in calculations with the 'tight' basis set. Calculations were performed on Athena (28 cores).

System	mol 1 (eV)	mol 2(eV)	total (eV)	E_{bind} (eV)	E_{bind} (eV)[3]	time(s)
formic acid dimer	-5171.6943962	-5171.6943962	-10344.2941896	-0.905	-0.803	10584.26
uracil dimer	-11303.3462932	-11303.3462932	-22607.6201696	-0.928	-0.856	67612.23
uracil dimer1 stack	-11303.3462932	-11303.3462932	-22607.2612571	-0.569	-0.456	45268.65

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