Supplemental Material for "Push it to the limit: comparing periodic and local approaches to density functional theory for intermolecular interactions"

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Contents

1 Overview

This document contains the supplementary material for the journal article "Push it to the limit: comparing periodic and local approaches to density functional theory for intermolecular interactions."

Herein we provide a handful of supplementary figures mentioned in the text.

There is also an Excel file (binding_energies.xls) that contains raw binding energies across the S22 dataset. This data has not been reproduced within this document.

2 Tables

2.1 Numbering convention

System Number	System Name
1	Ammonia dimer
2	Water dimer
3	Formic acid dimer
4	Formamide dimer
5	Uracil dimer h-bonded
6	2-pyridoxine 2-aminopyridine complex
7	Adenine thymine Watson-Crick complex
8	Methane dimer
9	Ethene dimer
10	Benzene - Methane complex
11	Benzene dimer parallel displaced
12	Pyrazine dimer
13	Uracil dimer stack
14	Indole benzene complex stack
15	Adenine thymine complex stack
16	Ethene ethyne complex
17	Benzene water complex
18	Benzene ammonia complex
19	Benzene HCN complex
20	Benzene dimer T-shaped
21	Indole benzene T-shape complex
22	Phenol dimer

Table 1: Numbering convention of S22 used to abbreviate systems in the remainder of the SM.

3 Figures

3.1 Convergence with wavefunction kinetic energy

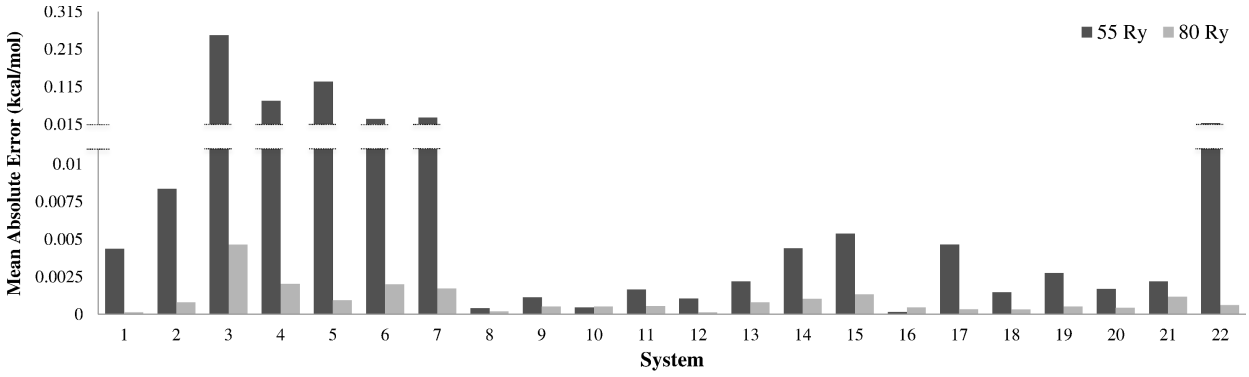


Figure 1: Convergence of SPW92 plane wave binding energies with respect to wavefunction kinetic energy cutoff. Errors are expressed relative to binding energies computed with a 110 Ry cutoff.

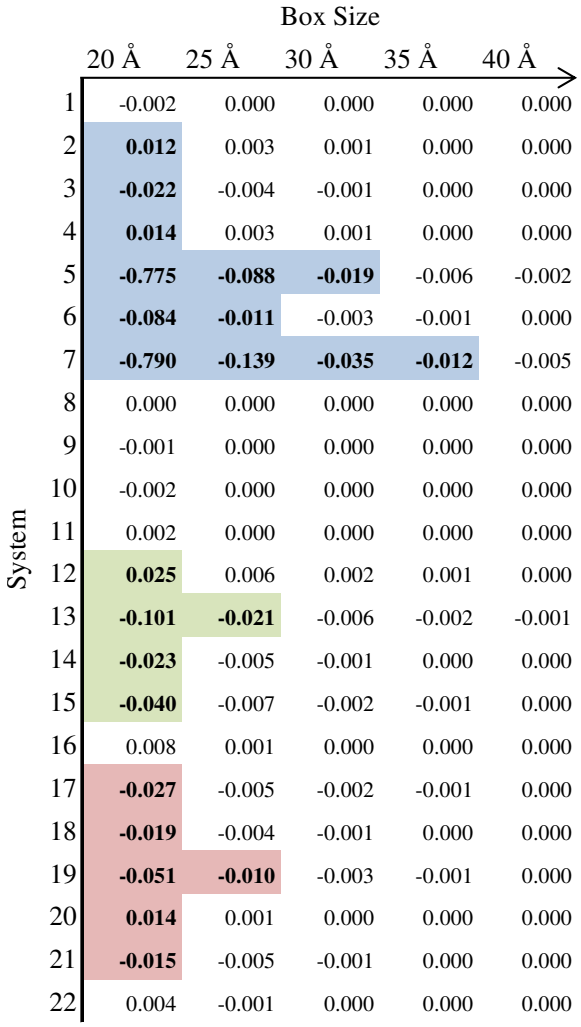
3.2 Convergence with box size

3.2.1 SPW92 without dipole correction

System	Box Size: 20 Å	25 Å	30 Å	35 Å	40 Å	45 Å
1	**-0.027**	**-0.009**	-0.004	-0.002	-0.001	-0.001
2	**0.012**	0.003	0.001	0.000	0.000	0.000
3	**-0.057**	**-0.017**	-0.007	-0.003	-0.002	-0.001
4	**-0.161**	**-0.059**	**-0.026**	**-0.013**	-0.008	-0.005
5	**-1.000**	**-0.167**	**-0.054**	**-0.024**	**-0.012**	-0.007
6	**-0.181**	**-0.045**	**-0.017**	-0.008	-0.005	-0.003
7	**-0.914**	**-0.179**	**-0.052**	**-0.021**	**-0.010**	-0.005
8	0.000	0.000	0.000	0.000	0.000	0.000
9	-0.001	0.000	0.000	0.000	0.000	0.000
10	-0.002	0.000	0.000	0.000	0.000	0.000
11	0.002	0.000	0.000	0.000	0.000	0.000
12	**0.025**	0.006	0.002	0.001	0.000	0.000
13	**-0.186**	**-0.052**	**-0.020**	**-0.009**	-0.005	-0.003
14	**-0.029**	-0.007	-0.002	-0.001	0.000	0.000
15	**-0.139**	**-0.042**	**-0.017**	-0.008	-0.005	-0.003
16	0.009	0.001	0.000	0.000	0.000	0.000
17	**-0.017**	-0.002	0.000	0.000	0.000	0.000
18	**-0.016**	-0.003	-0.001	0.000	0.000	0.000
19	**-0.014**	0.002	0.002	0.002	0.001	0.001
20	**0.015**	0.002	0.001	0.000	0.000	0.000
21	**0.017**	0.007	0.004	0.002	0.001	0.001
22	**0.052**	**0.015**	0.007	0.003	0.002	0.001

Figure 2: Convergence of SPW92 plane wave binding energies with respect to box size. The number in each cell corresponds to the change in binding energy (in kcal/mol) on increasing the box size by 5 Å to the listed size. Errors greater in magnitude than 0.009 kcal/mol are bold-faced and colored, with the cell color corresponding to the type of interaction. All calculations utilize a wavefunction kinetic energy cutoff of 80 Ry.

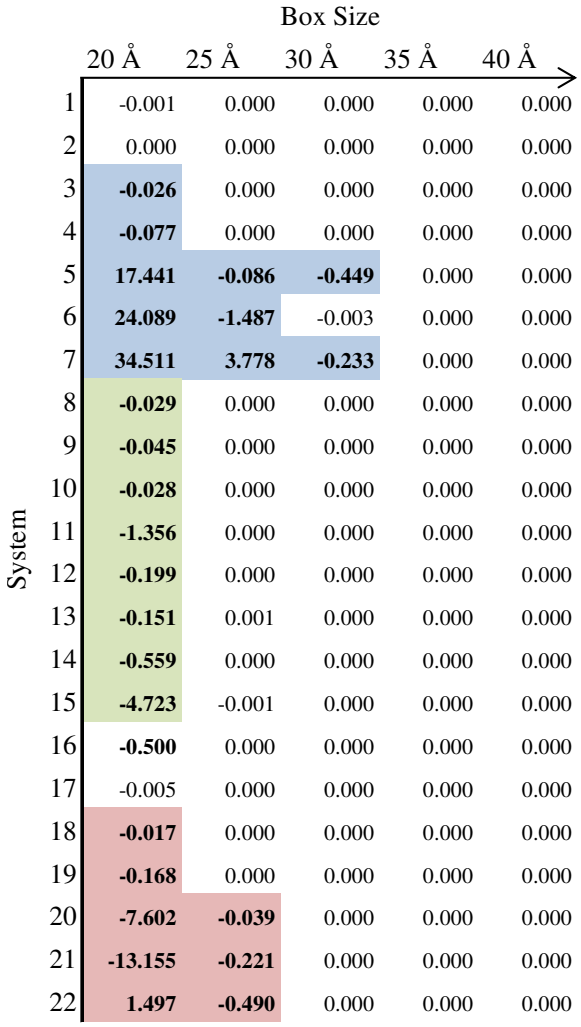
3.2.2 SPW92 with Makov-Payne correction



System	20 Å	25 Å	30 Å	35 Å	40 Å
1	-0.002	0.000	0.000	0.000	0.000
2	**0.012**	0.003	0.001	0.000	0.000
3	**-0.022**	-0.004	-0.001	0.000	0.000
4	**0.014**	0.003	0.001	0.000	0.000
5	**-0.775**	**-0.088**	**-0.019**	-0.006	-0.002
6	**-0.084**	**-0.011**	-0.003	-0.001	0.000
7	**-0.790**	**-0.139**	**-0.035**	**-0.012**	-0.005
8	0.000	0.000	0.000	0.000	0.000
9	-0.001	0.000	0.000	0.000	0.000
10	-0.002	0.000	0.000	0.000	0.000
11	0.002	0.000	0.000	0.000	0.000
12	**0.025**	0.006	0.002	0.001	0.000
13	**-0.101**	**-0.021**	-0.006	-0.002	-0.001
14	**-0.023**	-0.005	-0.001	0.000	0.000
15	**-0.040**	-0.007	-0.002	-0.001	0.000
16	0.008	0.001	0.000	0.000	0.000
17	**-0.027**	-0.005	-0.002	-0.001	0.000
18	**-0.019**	-0.004	-0.001	0.000	0.000
19	**-0.051**	**-0.010**	-0.003	-0.001	0.000
20	**0.014**	0.001	0.000	0.000	0.000
21	**-0.015**	-0.005	-0.001	0.000	0.000
22	0.004	-0.001	0.000	0.000	0.000

Figure 3: Convergence of SPW92 plane wave binding energies employing the Makov-Payne dipole correction with respect to box size. For further details, see Figure 2.

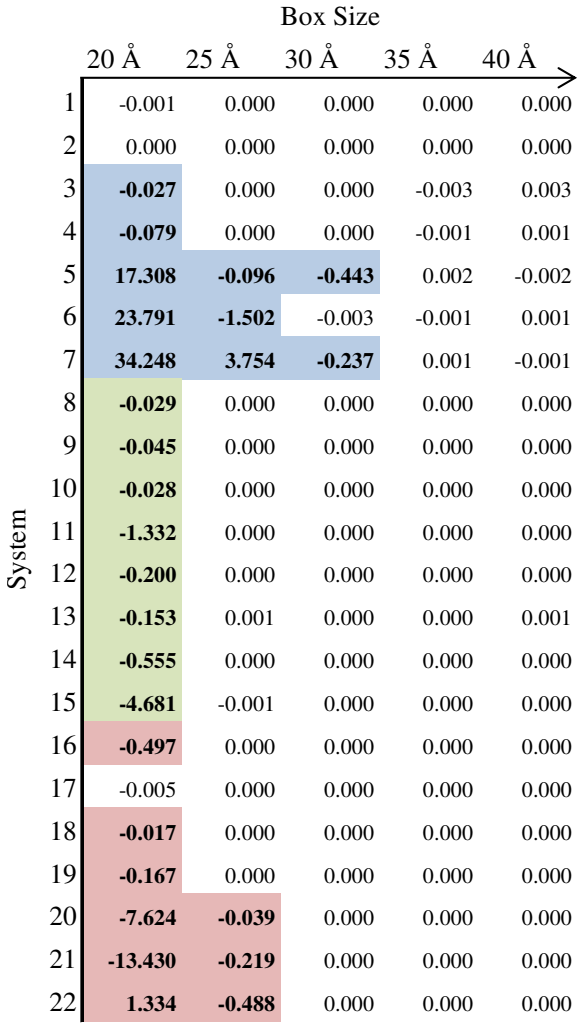
3.2.3 SPW92 with Martyna-Tuckerman correction



System	20 Å	25 Å	30 Å	35 Å	40 Å
1	-0.001	0.000	0.000	0.000	0.000
2	0.000	0.000	0.000	0.000	0.000
3	**-0.026**	0.000	0.000	0.000	0.000
4	**-0.077**	0.000	0.000	0.000	0.000
5	**17.441**	**-0.086**	**-0.449**	0.000	0.000
6	**24.089**	**-1.487**	-0.003	0.000	0.000
7	**34.511**	**3.778**	**-0.233**	0.000	0.000
8	**-0.029**	0.000	0.000	0.000	0.000
9	**-0.045**	0.000	0.000	0.000	0.000
10	**-0.028**	0.000	0.000	0.000	0.000
11	**-1.356**	0.000	0.000	0.000	0.000
12	**-0.199**	0.000	0.000	0.000	0.000
13	**-0.151**	0.001	0.000	0.000	0.000
14	**-0.559**	0.000	0.000	0.000	0.000
15	**-4.723**	-0.001	0.000	0.000	0.000
16	**-0.500**	0.000	0.000	0.000	0.000
17	-0.005	0.000	0.000	0.000	0.000
18	**-0.017**	0.000	0.000	0.000	0.000
19	**-0.168**	0.000	0.000	0.000	0.000
20	**-7.602**	**-0.039**	0.000	0.000	0.000
21	**-13.155**	**-0.221**	0.000	0.000	0.000
22	**1.497**	**-0.490**	0.000	0.000	0.000

Figure 4: Convergence of SPW92 plane wave binding energies employing the Martyna-Tuckerman dipole correction with respect to box size. For further details, see Figure 2.

3.2.4 PBE with Martyna-Tuckerman correction



System	20 Å	25 Å	30 Å	35 Å	40 Å
1	-0.001	0.000	0.000	0.000	0.000
2	0.000	0.000	0.000	0.000	0.000
3	**-0.027**	0.000	0.000	-0.003	0.003
4	**-0.079**	0.000	0.000	-0.001	0.001
5	**17.308**	**-0.096**	**-0.443**	0.002	-0.002
6	**23.791**	**-1.502**	-0.003	-0.001	0.001
7	**34.248**	**3.754**	**-0.237**	0.001	-0.001
8	**-0.029**	0.000	0.000	0.000	0.000
9	**-0.045**	0.000	0.000	0.000	0.000
10	**-0.028**	0.000	0.000	0.000	0.000
11	**-1.332**	0.000	0.000	0.000	0.000
12	**-0.200**	0.000	0.000	0.000	0.000
13	**-0.153**	0.001	0.000	0.000	0.001
14	**-0.555**	0.000	0.000	0.000	0.000
15	**-4.681**	-0.001	0.000	0.000	0.000
16	**-0.497**	0.000	0.000	0.000	0.000
17	-0.005	0.000	0.000	0.000	0.000
18	**-0.017**	0.000	0.000	0.000	0.000
19	**-0.167**	0.000	0.000	0.000	0.000
20	**-7.624**	**-0.039**	0.000	0.000	0.000
21	**-13.430**	**-0.219**	0.000	0.000	0.000
22	**1.334**	**-0.488**	0.000	0.000	0.000

Figure 5: Convergence of PBE plane wave binding energies employing the Martyna-Tuckerman dipole correction with respect to box size. For further details, see Figure 2.

3.3 Convergence with vacuum distance

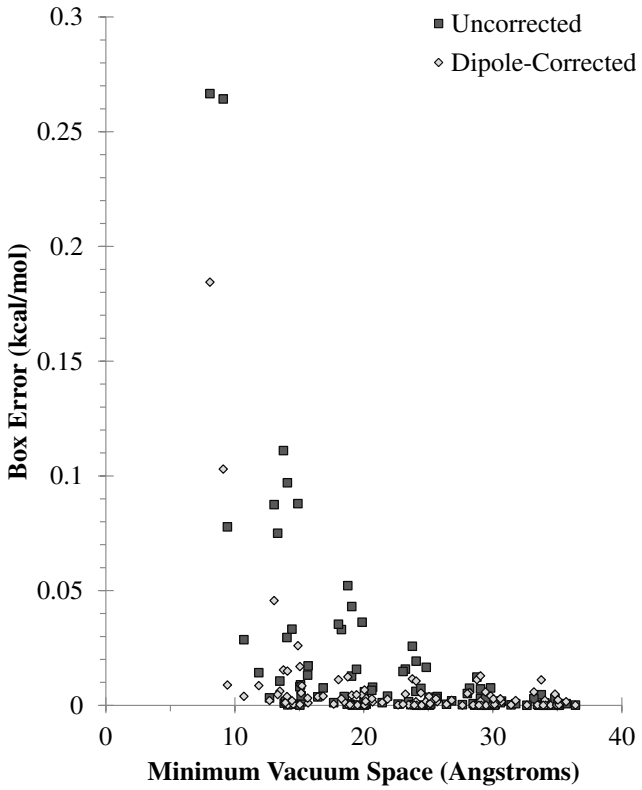


Figure 6: Convergence of SPW92 plane wave binding energies with and without the Makov-Payne dipole correction with respect to the closest system-image contact distances.