Establishing the accuracy of density functional approaches for the description of noncovalent interactions in ionic liquids

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Supplementary Information

Comparison of calculations using plane-wave and gaussian-type orbital basis set

To conduct a careful comparison between plane-wave basis set and gaussian-type orbital (GTO) basis set data, we further examined how the DFT-PBE energies from plane-wave and GTO basis set calculations can change the vdW-corrected DFT methods by adding the dispersion correction energy to the Gaussian-type PBE energy,

$$
\begin{aligned}
E_{\text{PBE+vdW}}^{\text{Gaussian}} &= E_{\text{PBE}}^{\text{Gaussian}} + E_{\text{disp}} \\
&= E_{\text{PBE}}^{\text{Gaussian}} + E_{\text{PBE+vdW}}^{\text{plane−wave}} - E_{\text{PBE}}^{\text{plane−wave}}
\end{aligned}
$$

As shown in Table S1, according to the comparison with plane-wave vdW-corrected PBE energy, $E_{\text{PBE+vdW}}^{\text{plane−wave}}$, both MADs from different types of basis sets differ by 0.46 kJ/mol (0.12 % in MAPDs) at most among the tested vdW-corrected DFT methods, proving that it is reliable to compare the plane-wave vdW-corrected DFT energies with the GTO-based calculations.

Table S1: Mean absolute deviation (MAD, kJ/mol) of the vdW-corrected DFT methods based on calculations using plane-wave basis set, $E_{\text{PBE+vdW}}^{\text{plane−wave}}$, and Gaussian-type basis set, $E_{\text{PBE+vdW}}^{\text{Gaussian}} = E_{\text{PBE+vdW}}^{\text{plane−wave}} - E_{\text{PBE}}^{\text{plane−wave}} + E_{\text{PBE}}^{\text{Gaussian}}$.

MAD (kJ/mol)	$E_{\text{PBE+vdW}}^{\text{plane−wave}}$	$E_{\text{PBE+vdW}}^{\text{Gaussian}}$	$E_{\text{PBE+vdW}}^{\text{plane−wave}}$	$E_{\text{PBE+vdW}}^{\text{Gaussian}}$
	MAD (kJ/mol)		MAPD (%)	
PBE	16.71	16.13	4.58	4.42
D3(BJ)	4.89	4.67	1.29	1.24
TS	3.59	3.65	0.96	0.98
TS/HI	4.69	4.30	1.26	1.15
TS+SCS	3.84	3.82	1.03	1.03
MBD@rsSCS	4.42	4.48	1.17	1.20
MBD@rsSCS/FI	4.27	4.35	1.14	1.17
uMBD	4.08	4.26	1.09	1.10

Table S2: Mean absolute deviation (MAD, kJ/mol), mean signed deviation (MSD, kJ/mol) and mean absolute percentage deviation (MAPD, %) of the tested methods in ionic liquid benchmark set.

	MAD (kJ/mol)	MSD (kJ/mol)	MAPD (%)
PBE and vdW-correction methods			
PBE	16.71	+16.70	4.58
D3(BJ)	4.89	+0.95	1.29
TS	3.59	+1.20	0.96
TS/HI	4.69	+3.20	1.26
TS+SCS	3.84	+2.04	1.03
MBD@rsSCS	4.42	-0.50	1.17
MBD@rsSCS/FI	4.27	-0.25	1.14
uMBD	4.08	-2.03	1.09
Nonlocal vdW functionals			
vdW-DF2	3.82	+3.48	1.01
rev-vdW-DF2	2.92	+0.40	0.77
vdW-DF-cx	3.03	+0.29	0.80
SCAN+rVV10	3.67	-3.28	0.98
Range-separated hybrid functional			
ωB97X-V	2.07	+0.96	0.56
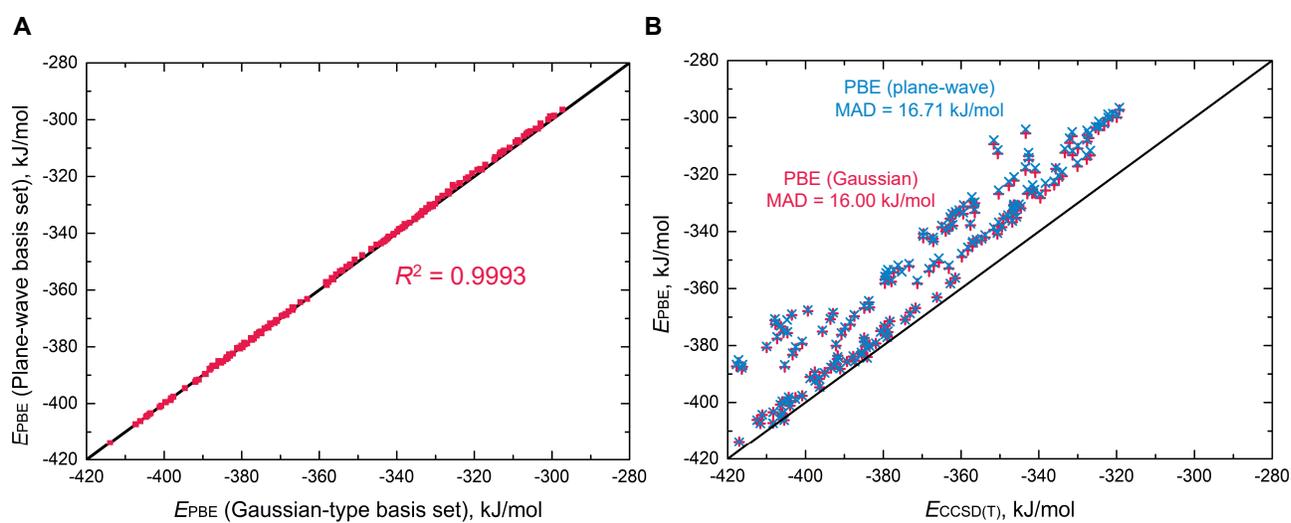
Figure S1: **A** PBE interaction energy of ionic liquid pairs in the IL174 benchmark set by using Gaussian-type basis set in Gaussian09 (*x*-axis) and plane-wave basis set in VASP (*y*-axis) in kJ/mol. **B** CCSD(T) (*x*-axis) and PBE (*y*-axis) interaction energies of ionic liquid pairs by using Gaussian-type basis set (red) and plane-wave basis set (blue) in kJ/mol.
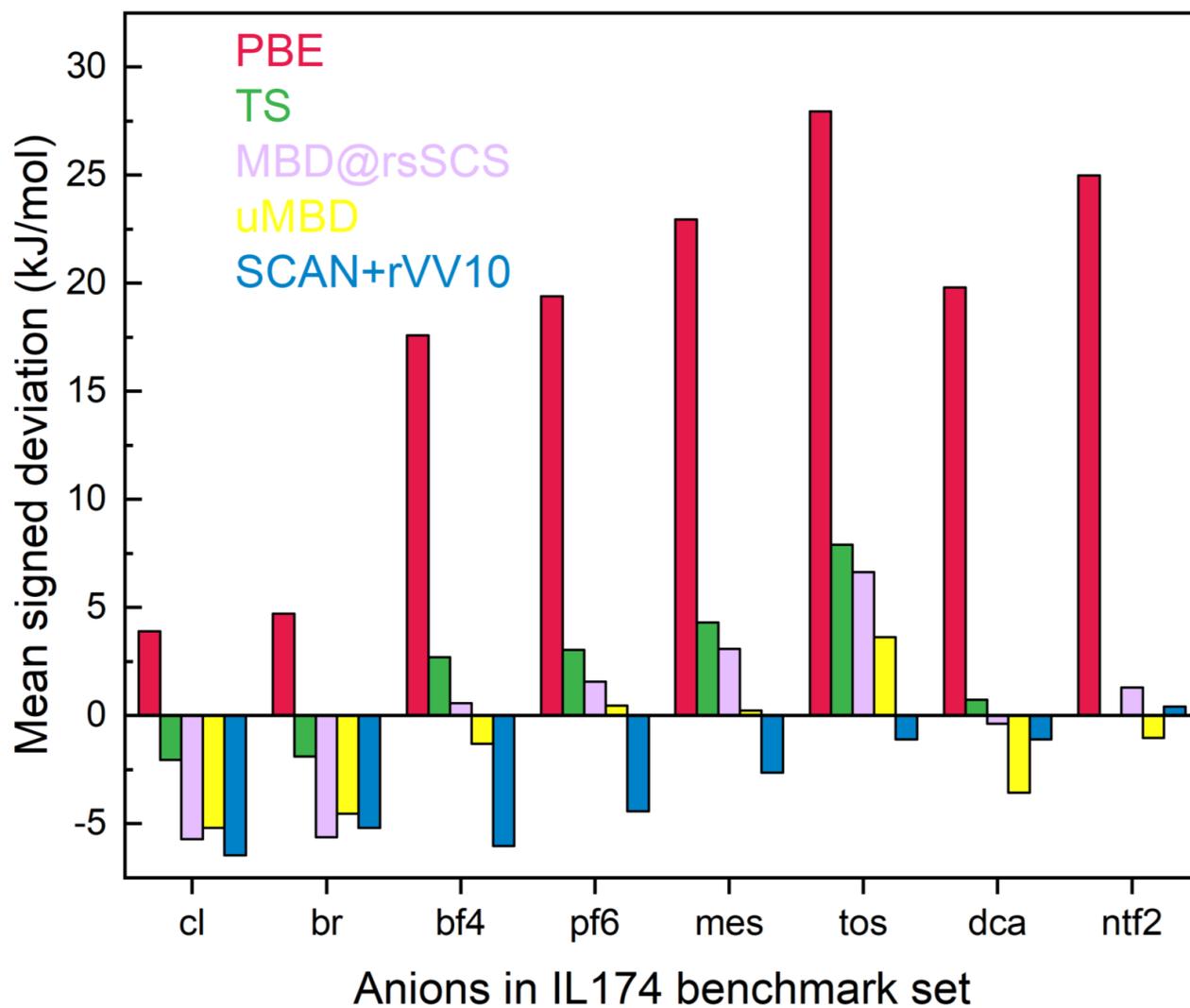
Figure S2: Mean signed deviations (MSDs, in kJ/mol) of PBE and some van der Waals approaches tested for the ionic liquid pairs in the IL174 benchmark set as grouped by the type of their anions.