

# Supporting Information for “Accurate Description of Intermolecular Interactions Involving Ions Using Symmetry-Adapted Perturbation Theory”

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## Summary

- Errors engendered by the single-exchange approximation (SEA) for various exchange energies terms are listed in Table S1 (aDZ basis set) and Table S2 (aQZ basis set). These should be compared to the aTZ results in Table III of the paper.
- For the AHB21 data set, the  $\delta$ MP2 correction as well as the scaled-exchange corrections  $[p_{\text{ex}}(\alpha = 2) - 1]E_{\text{exch-ind,resp}}^{(20)}$  and  $[p_{\text{ex}}(\alpha = 2) - 1]^t E_{\text{exch-ind}}^{(22)}$  are shown in Figure S1 (aDZ basis set) and Figure S2 (aQZ basis set). These should be compared to the aTZ results in Fig. 3 of the paper.
- For the CHB6 data set, the  $\delta$ MP2 correction as well as the scaled-exchange corrections  $[p_{\text{ex}}(\alpha = 2) - 1]E_{\text{exch-ind,resp}}^{(20)}$  and  $[p_{\text{ex}}(\alpha = 2) - 1]^t E_{\text{exch-ind}}^{(22)}$  are shown in Figure S3 (aDZ basis set) and Figure S4 (aQZ basis set). These should be compared to the aTZ results in Fig. 3 of the paper.
- Table S3 shows the performance of the SAPT2+3- $\delta$ MP2/aug-cc-pVXZ method (for X = D, T, Q), as applied to AHB21, for different versions of the scaling of the second-order exchange energies. These varieties include no scaling at all, or else  $\alpha = 1$  or  $\alpha = 3$  in Eq. (4) of the paper. For comparison, with the aTZ basis the value  $\alpha = 2$  affords a MAE of 0.49 kcal/mol (see Table IV).

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TABLE S1: Mean absolute errors (MAEs) and maximum errors in exchange energies based on HF-SAPT/aDZ and DFT-SAPT/aDZ with the  $S^2$  approximation for the AHB21 and CHB6 data sets, with respect to exchange energies without the  $S^2$  approximation.

Exchange Term	error / kcal mol <sup>-1</sup>		
	MAE	Maximum	
		value	system
<b>— AHB21 —</b>			
<b><u>HF-SAPT</u></b>			
$E_{\text{exch}}^{(10)}(S^2)$	1.04	6.31	Cl <sup>-</sup> (HCl)
$E_{\text{exch-ind,resp}}^{(20)}(S^2)$	1.01	8.22	Cl <sup>-</sup> (HCl)
$p_{\text{ex}}(\alpha = 2.07)E_{\text{exch-ind,resp}}^{(20)}(S^2)$	0.08	0.36	F <sup>-</sup> (HF)
$E_{\text{exch-disp}}^{(20)}(S^2)$	0.07	0.35	F <sup>-</sup> (HF)
$tE_{\text{exch-ind}}^{(22)}(S^2)$	0.13	0.63	Cl <sup>-</sup> (HCl)
$p_{\text{ex}}(\alpha = 2)tE_{\text{exch-ind}}^{(22)}(S^2)$	0.01	0.09	F <sup>-</sup> (HF)
<b><u>DFT-SAPT</u></b>			
$E_{\text{exch}}^{(1)}(S^2)$	1.14	6.30	Cl <sup>-</sup> (HCl)
$E_{\text{exch-ind}}^{(2)}(S^2)$	1.27	9.02	Cl <sup>-</sup> (HCl)
$p_{\text{ex}}(\alpha = 2.06)E_{\text{exch-ind}}^{(2)}(S^2)$	0.09	0.61	Cl <sup>-</sup> (HCl)
$E_{\text{exch-disp}}^{(2)}(S^2)$	0.12	0.53	F <sup>-</sup> (HF)
<b>— CHB6 —</b>			
<b><u>HF-SAPT</u></b>			
$E_{\text{exch}}^{(10)}(S^2)$	0.03	0.05	Li <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$E_{\text{exch-ind,resp}}^{(20)}(S^2)$	0.06	0.08	Li <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$p_{\text{ex}}(\alpha = 2.20)E_{\text{exch-ind,resp}}^{(20)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$E_{\text{exch-disp}}^{(20)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$tE_{\text{exch-ind}}^{(22)}(S^2)$	0.00	0.01	K <sup>+</sup> (H <sub>2</sub> O)
$p_{\text{ex}}(\alpha = 2)tE_{\text{exch-ind}}^{(22)}(S^2)$	0.00	0.01	Li <sup>+</sup> (H <sub>2</sub> O)
<b><u>DFT-SAPT</u></b>			
$E_{\text{exch}}^{(1)}(S^2)$	0.03	0.05	Li <sup>+</sup> (H <sub>2</sub> O)
$E_{\text{exch-ind}}^{(2)}(S^2)$	0.06	0.08	Li <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$p_{\text{ex}}(\alpha = 2.19)E_{\text{exch-ind}}^{(2)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$E_{\text{exch-disp}}^{(2)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )

TABLE S2: Mean absolute errors (MAEs) and maximum errors in exchange energies based on HF-SAPT/aQZ and DFT-SAPT/aQZ with the  $S^2$  approximation for the AHB21 and CHB6 data sets, with respect to exchange energies without the  $S^2$  approximation.

Exchange Term	error / kcal mol <sup>-1</sup>		
	MAE	Maximum	
		value	system
<b>— AHB21 —</b>			
<b>HF-SAPT</b>			
$E_{\text{exch}}^{(10)}(S^2)$	1.05	6.36	Cl <sup>-</sup> (HCl)
$E_{\text{exch-ind,resp}}^{(20)}(S^2)$	1.06	8.51	Cl <sup>-</sup> (HCl)
$p_{\text{ex}}(\alpha = 2.04)E_{\text{exch-ind,resp}}^{(20)}(S^2)$	0.07	0.31	F <sup>-</sup> (HF)
$E_{\text{exch-disp}}^{(20)}(S^2)$	0.07	0.35	F <sup>-</sup> (HF)
$tE_{\text{exch-ind}}^{(22)}(S^2)$	0.09	0.47	F <sup>-</sup> (HF)
$p_{\text{ex}}(\alpha = 2)tE_{\text{exch-ind}}^{(22)}(S^2)$	0.01	0.06	F <sup>-</sup> (HF)
<b>DFT-SAPT</b>			
$E_{\text{exch}}^{(1)}(S^2)$	1.15	6.32	Cl <sup>-</sup> (HCl)
$E_{\text{exch-ind}}^{(2)}(S^2)$	1.33	9.34	Cl <sup>-</sup> (HCl)
$p_{\text{ex}}(\alpha = 2.07)E_{\text{exch-ind}}^{(2)}(S^2)$	0.09	0.84	Cl <sup>-</sup> (HCl)
$E_{\text{exch-disp}}^{(2)}(S^2)$	0.11	0.51	F <sup>-</sup> (HF)
<b>— CHB6 —</b>			
<b>HF-SAPT</b>			
$E_{\text{exch}}^{(10)}(S^2)$	0.03	0.05	Li <sup>+</sup> (H <sub>2</sub> O)
$E_{\text{exch-ind,resp}}^{(20)}(S^2)$	0.06	0.10	Li <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$p_{\text{ex}}(\alpha = 2.19)E_{\text{exch-ind,resp}}^{(20)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$E_{\text{exch-disp}}^{(20)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$tE_{\text{exch-ind}}^{(22)}(S^2)$	0.00	0.01	K <sup>+</sup> (H <sub>2</sub> O)
$p_{\text{ex}}(\alpha = 2)tE_{\text{exch-ind}}^{(22)}(S^2)$	0.00	0.00	Li <sup>+</sup> (H <sub>2</sub> O)
<b>DFT-SAPT</b>			
$E_{\text{exch}}^{(1)}(S^2)$	0.03	0.06	Li <sup>+</sup> (H <sub>2</sub> O)
$E_{\text{exch-ind}}^{(2)}(S^2)$	0.07	0.10	Li <sup>+</sup> (H <sub>2</sub> O)
$p_{\text{ex}}(\alpha = 2.19)E_{\text{exch-ind}}^{(2)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )
$E_{\text{exch-disp}}^{(2)}(S^2)$	0.00	0.01	K <sup>+</sup> (C <sub>6</sub> H <sub>6</sub> )

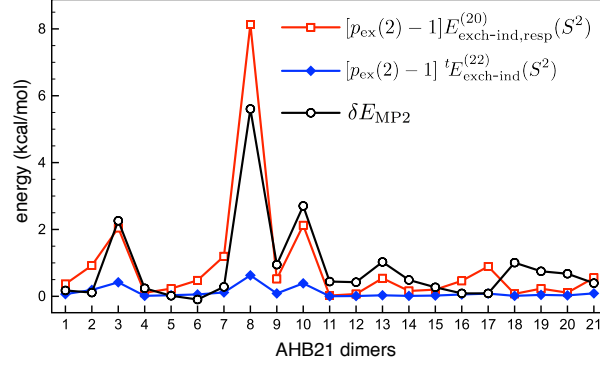


FIG. S1: Magnitude of the  $\delta$ MP2 correction and the scaled-exchange corrections  $[p_{\text{ex}}(2.0) - 1]E_{\text{exch-ind,resp}}^{(20)}$  and  $[p_{\text{ex}}(2.0) - 1]^tE_{\text{exch-ind}}^{(22)}$ , for the AHB21 data set using the aDZ basis set.

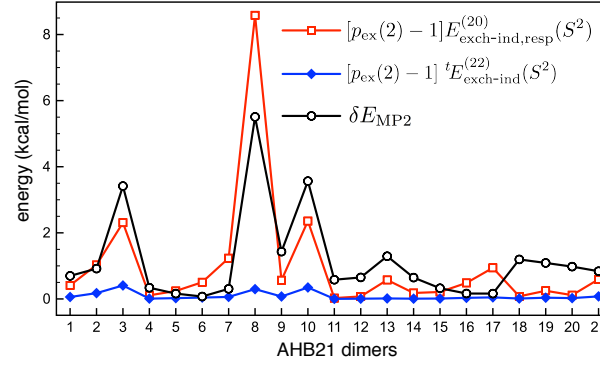


FIG. S2: Magnitude of the  $\delta$ MP2 correction and the scaled-exchange corrections  $[p_{\text{ex}}(2.0) - 1]E_{\text{exch-ind,resp}}^{(20)}$  and  $[p_{\text{ex}}(2.0) - 1]^tE_{\text{exch-ind}}^{(22)}$ , for the AHB21 data set using the aQZ basis set.

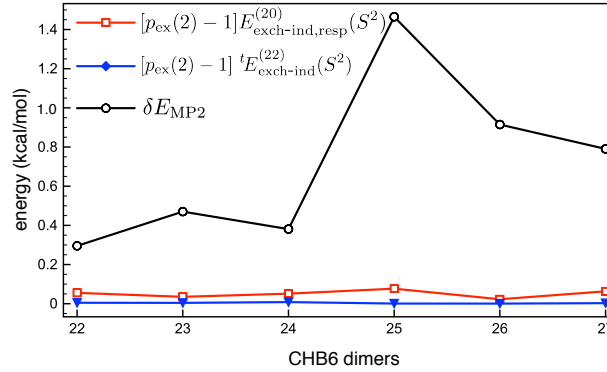


FIG. S3: Magnitude of the  $\delta$ MP2 correction, the exchange correction  $[p_{\text{ex}}(\alpha) - 1]E_{\text{exch-ind,resp}}^{(20)}$ , and  $[p_{\text{ex}}(\alpha) - 1]^tE_{\text{exch-ind}}^{(22)}$ , where  $p_{\text{ex}}(\alpha)$  is the scaling factor and  $\alpha = 2$  is employed, for the CHB6 data set, using the aDZ basis set.

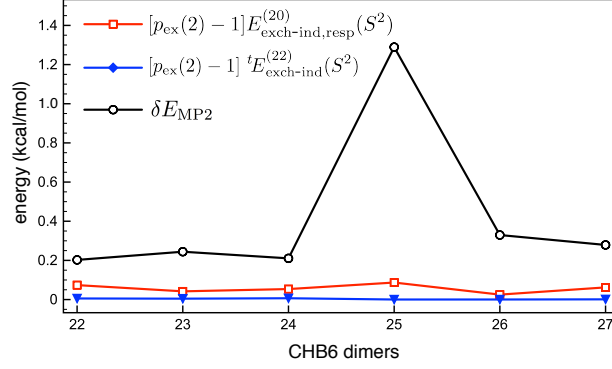


FIG. S4: Magnitude of the  $\delta\text{MP2}$  correction, the exchange correction  $[p_{\text{ex}}(\alpha) - 1]E_{\text{exch-ind,resp}}^{(20)}$ , and  $[p_{\text{ex}}(\alpha) - 1]^tE_{\text{exch-ind}}^{(22)}$ , where  $p_{\text{ex}}(\alpha)$  is the scaling factor and  $\alpha = 2$  is employed, for the CHB6 data set, using the aQZ basis set.

TABLE S3: MAEs (in kcal/mol) for the AHB21 data set computed at the SAPT2+3- $\delta\text{MP2}$  level with different scaled versions of the exchange corrections  $E_{\text{exch-ind,resp}}^{(20)}$  and  ${}^tE_{\text{exch-ind}}^{(22)}$ .

Basis Set	all AHB21			X <sup>-</sup> ... H <sup>+</sup> ... X <sup>-</sup> only		
	no scaling	$\alpha = 1$	$\alpha = 3$	no scaling	$\alpha = 1$	$\alpha = 3$
aDZ	0.96	1.03	1.17	1.00	1.24	1.76
aTZ	0.49	0.45	0.36	1.80	1.54	0.96
aQZ	0.73	0.66	0.53	2.63	2.35	1.73