Supporting information for “Breakdown of the single-exchange approximation in third-order symmetry-adapted perturbation theory”

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S1 CCSD(T)/CBS benchmarks

S1.1 Helium dimer

The CCSD(T) single-point energy calculations were carried out at each point on potential energy curves using the aug-cc-pVTZ (aTZ) and aug-cc-pVQZ (aQZ) basis sets. Then the CCSD(T) interaction energies calculated by both basis sets were extrapolated to the complete basis set (CBS) limit by using the two-point scheme suggested by Halkier *et al.*:[1,2]

$$E_{\mathrm{CBS}}(X,Y) = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3} \tag{S1}$$

where $X = 4$ (aQZ) and $Y = 3$ (aTZ) in this case.

S1.2 Anion–water and water–water dimers

In this case, MP2/aTZ and MP2/aQZ single-point energy calculations were carried out at each point on the potential energy curves and extrapolated to the CBS limit using Eq. (S1). From these MP2/CBS energies, a triples correction was estimated by comparing MP2 and CCSD(T) results in the

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aug-cc-pVTZ basis set. The CCSD(T)/CBS result is thus estimated according to

$$E_{\mathrm{CBS}}[\mathrm{CCSD(T)}] = E_{\mathrm{CBS}}[\mathrm{MP2}] + E_{\mathrm{aTZ}}[\mathrm{CCSD(T)}] - E_{\mathrm{aTZ}}[\mathrm{MP2}] \ . \tag{S2}$$

This procedure is based on the assumption that the difference between interaction energies by CCSD(T) and MP2 converges rapidly with respect to basis set.

S2 Additional figures

A variety of potential energy curves for $F^-(H_2O)$ were presented in the paper. Below, we plot all of the same quantities for $Cl^-(H_2O)$, $HO^-(H_2O)$, $(H_2O)_2$, and He_2.

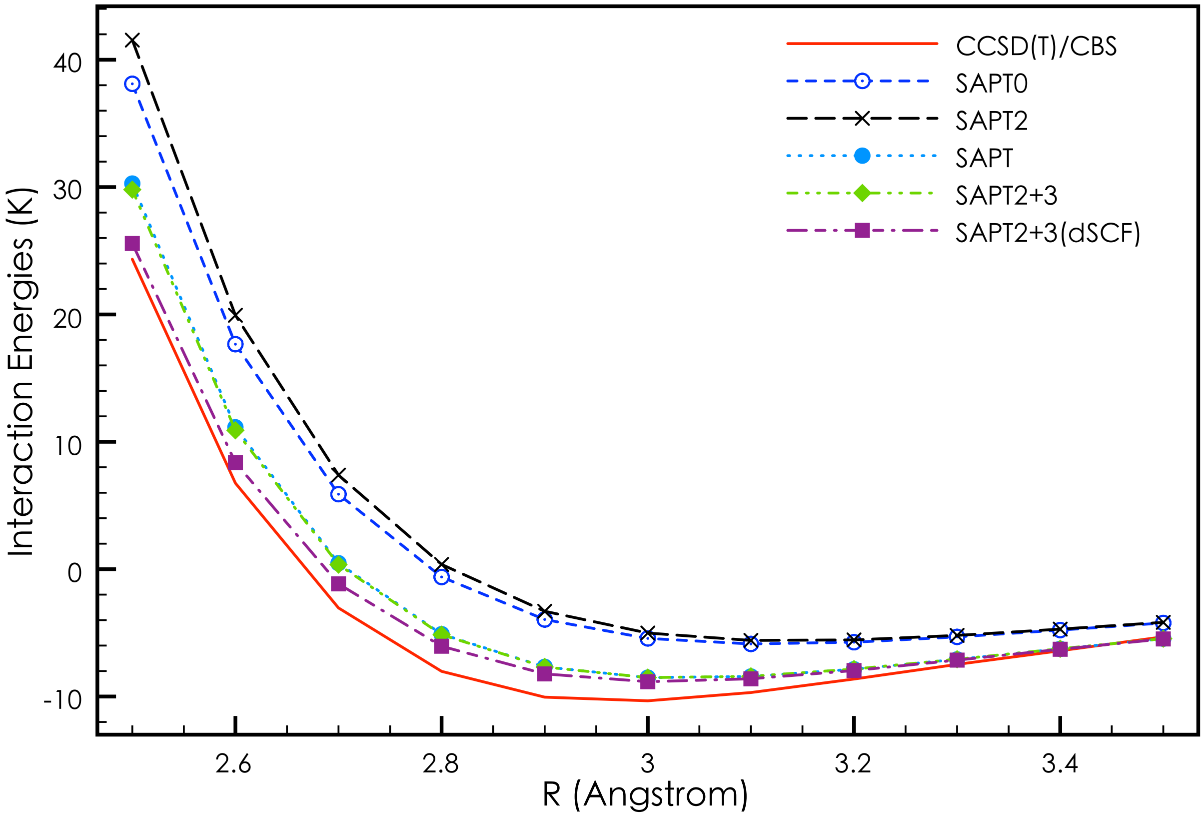

Figure S1: Comparison of performance of different levels of SAPT on the He $\cdots$ He system. SAPT2+3_dSCF means the interaction energies are calculated at the SAPT2+3 level with $E_{\mathrm{ind}}^{(30)}$ and $E_{\mathrm{exch-ind}}^{(30)}$ substituted by $\delta E_{\mathrm{int}}^{(2)}$. R is the distance between two helium atoms.

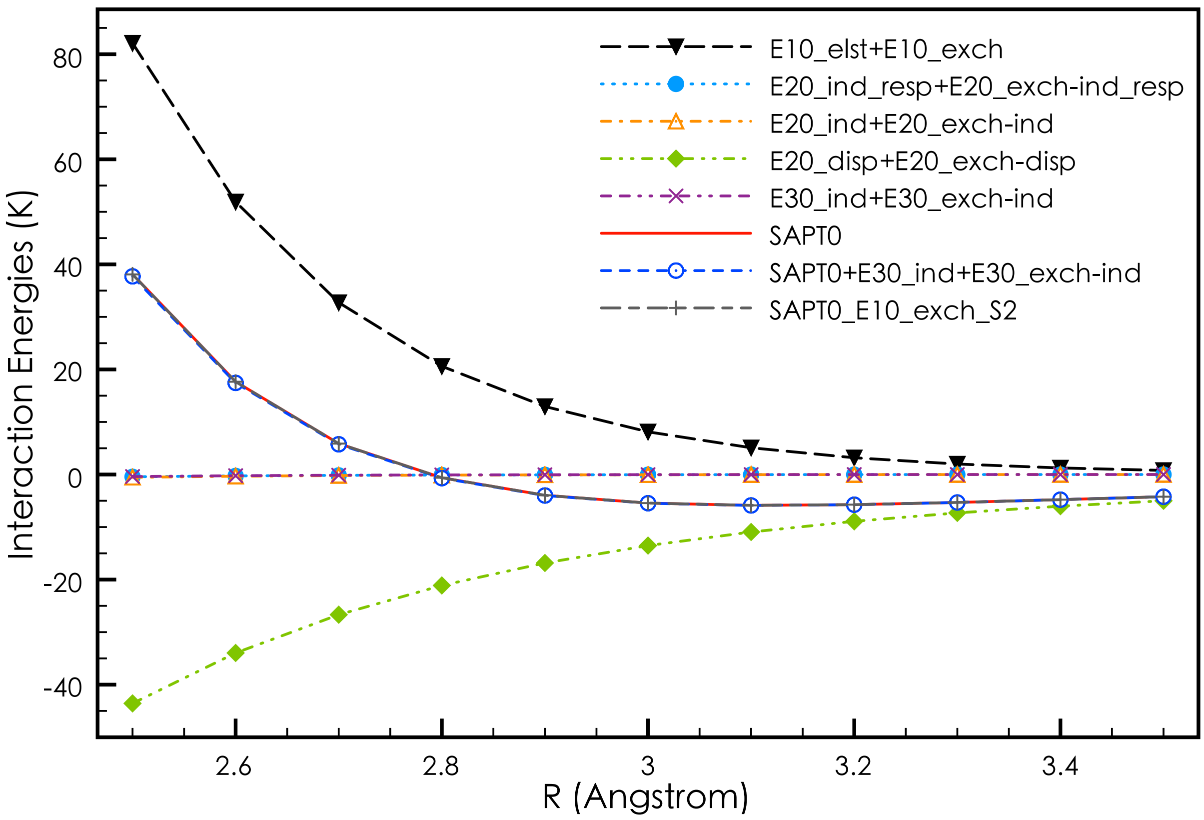

Figure S2: SAPT decomposition of the interaction energy of the He $\cdots$ He system into different orders of electrostatic (elst), induction (ind), and dispersion (disp) with their corresponding exchange (exch) contributions. SAPT0+E30_ind+E30_exch-ind means the interaction energies are calculated at the SAPT0 level plus $E^{(30)}_{\text{ind}}$ and $E^{(30)}_{\text{exch-ind}}$. R is the distance between two helium atoms.

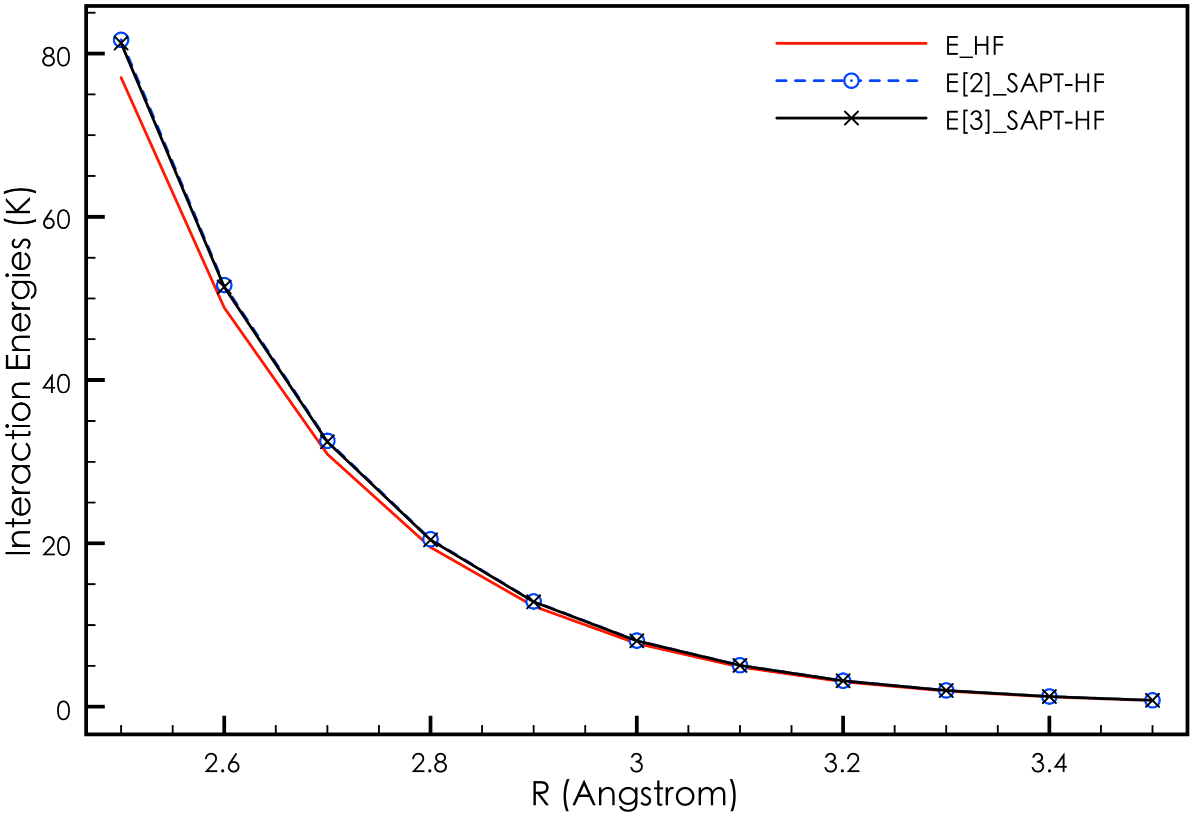

Figure S3: The supermolecular Hatree-Fock interaction energies $E_{\mathrm{int}}^{\mathrm{HF}}$ and approximate Hartree-Fock interaction energies composed by SAPT terms in second ($E_{\mathrm{SAPT-HF}}^{[2]}$) and third ($E_{\mathrm{SAPT-HF}}^{[2]}$) order for He $\cdots$ He system. R is the distance between two helium atoms.

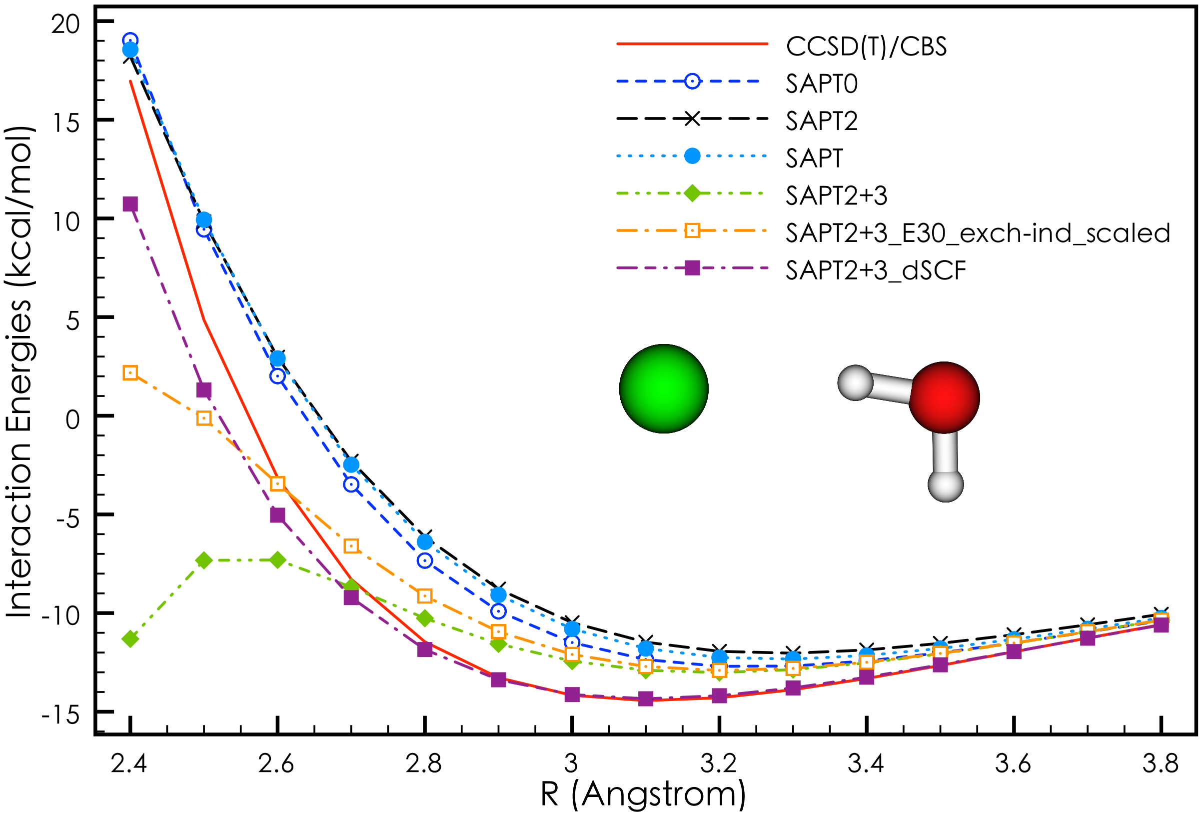

Figure S4: Comparison of performance of different levels of SAPT on the $\mathrm{Cl}^- \cdots \mathrm{H_2O}$ system. SAPT2+3_E30_exch-ind_scaled means the interaction energies are calculated at the SAPT2+3 level with $E^{(30)}_{\mathrm{exch-ind}}$ scaled by Eq. (7). SAPT2+3_dSCF means the interaction energies are calculated at the SAPT2+3 level with $E^{(30)}_{\mathrm{ind}}$ and $E^{(30)}_{\mathrm{exch-ind}}$ substituted by $\delta E^{(2)}_{\mathrm{int}}$. R is the distance between chloride and oxygen atom.

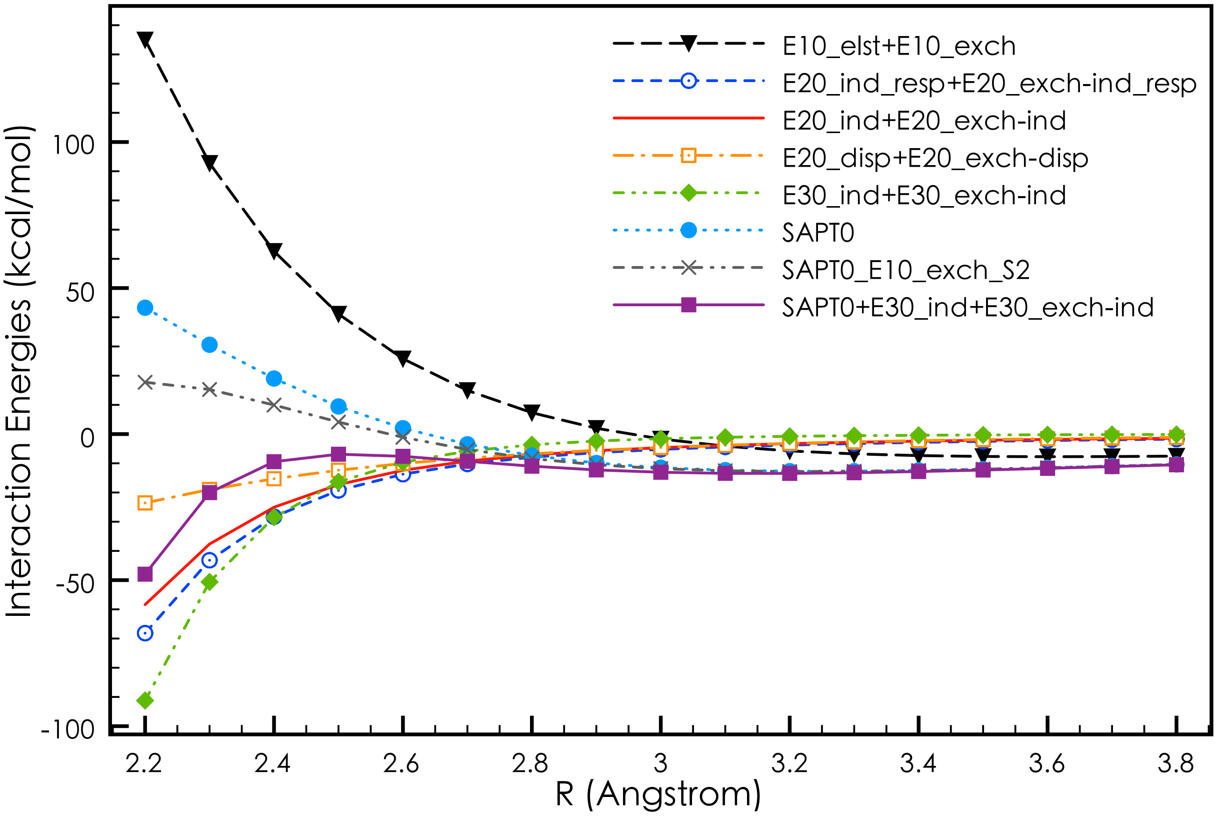

Figure S5: SAPT decomposition of the interaction energy of the $Cl^- \cdots H_2O$ system into different orders of electrostatic (elst), induction (ind), and dispersion (disp) with their corresponding exchange (exch) contributions. SAPT0+E30_ind+E30_exch-ind means the interaction energies are calculated at the SAPT0 level plus $E^{(30)}_{\mathrm{ind}}$ and $E^{(30)}_{\mathrm{exch-ind}}$. R is the distance between chloride and oxygen atom.

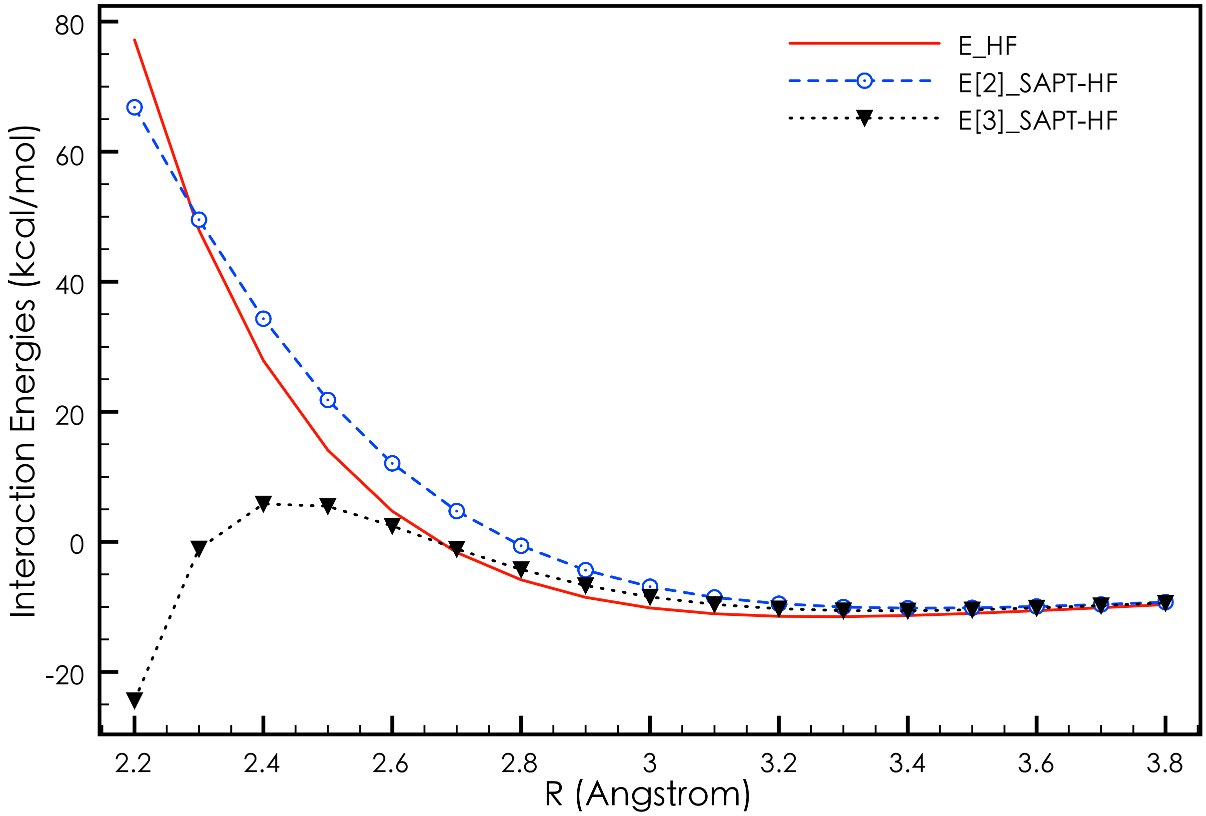

Figure S6: The supermolecular Hatree-Fock interaction energies $E_{\mathrm{int}}^{\mathrm{HF}}$ and approximate Hartree-Fock interaction energies composed by SAPT terms in second ($E_{\mathrm{SAPT-HF}}^{[2]}$) and third ($E_{\mathrm{SAPT-HF}}^{[2]}$) order for $\mathrm{Cl}^- \cdots \mathrm{H_2O}$ system. R is the distance between chloride and oxygen atom.

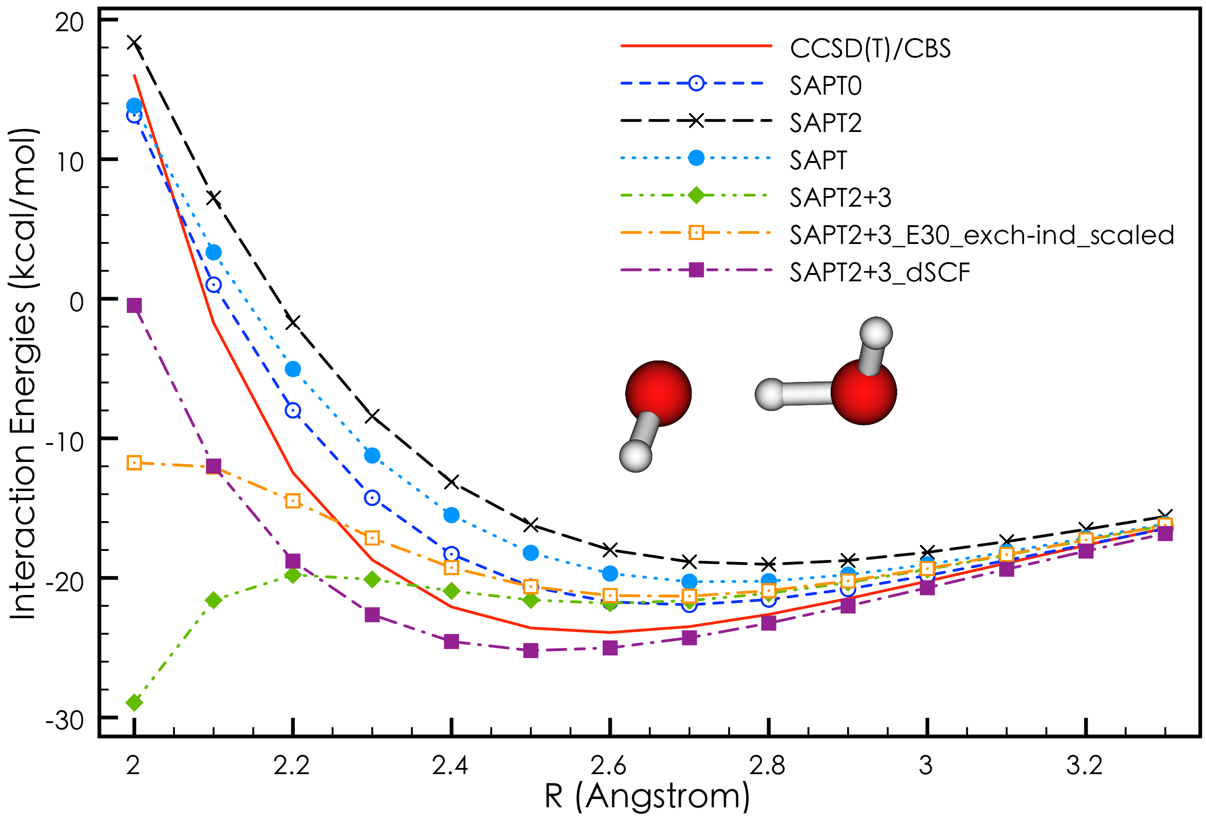

Figure S7: Comparison of performance of different levels of SAPT on the $OH^- \cdots H_2O$ system. SAPT2+3_E30_exch-ind_scaled means the interaction energies are calculated at the SAPT2+3 level with $E^{(30)}_{\text{exch-ind}}$ scaled by Eq. (7). SAPT2+3_dSCF means the interaction energies are calculated at the SAPT2+3 level with $E^{(30)}_{\text{ind}}$ and $E^{(30)}_{\text{exch-ind}}$ substituted by $\delta E^{(2)}_{\text{int}}$. R is the distance between two oxygen atoms.

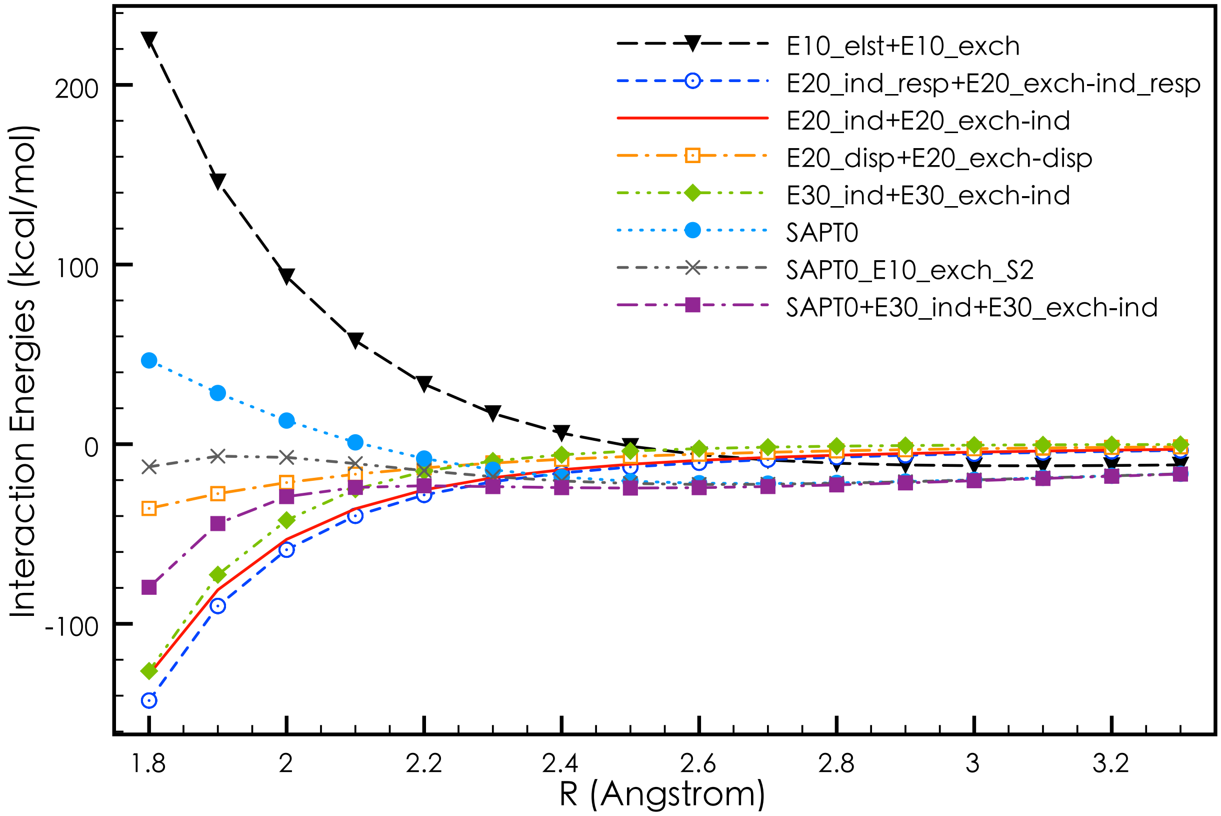

Figure S8: SAPT decomposition of the interaction energy of the $OH^- \cdots H_2O$ system into different orders of electrostatic (elst), induction (ind), and dispersion (disp) with their corresponding exchange (exch) contributions. SAPT0+E30_ind+E30_exch-ind means the interaction energies are calculated at the SAPT0 level plus $E^{(30)}_{\mathrm{ind}}$ and $E^{(30)}_{\mathrm{exch-ind}}$. R is the distance between two oxygen atoms.

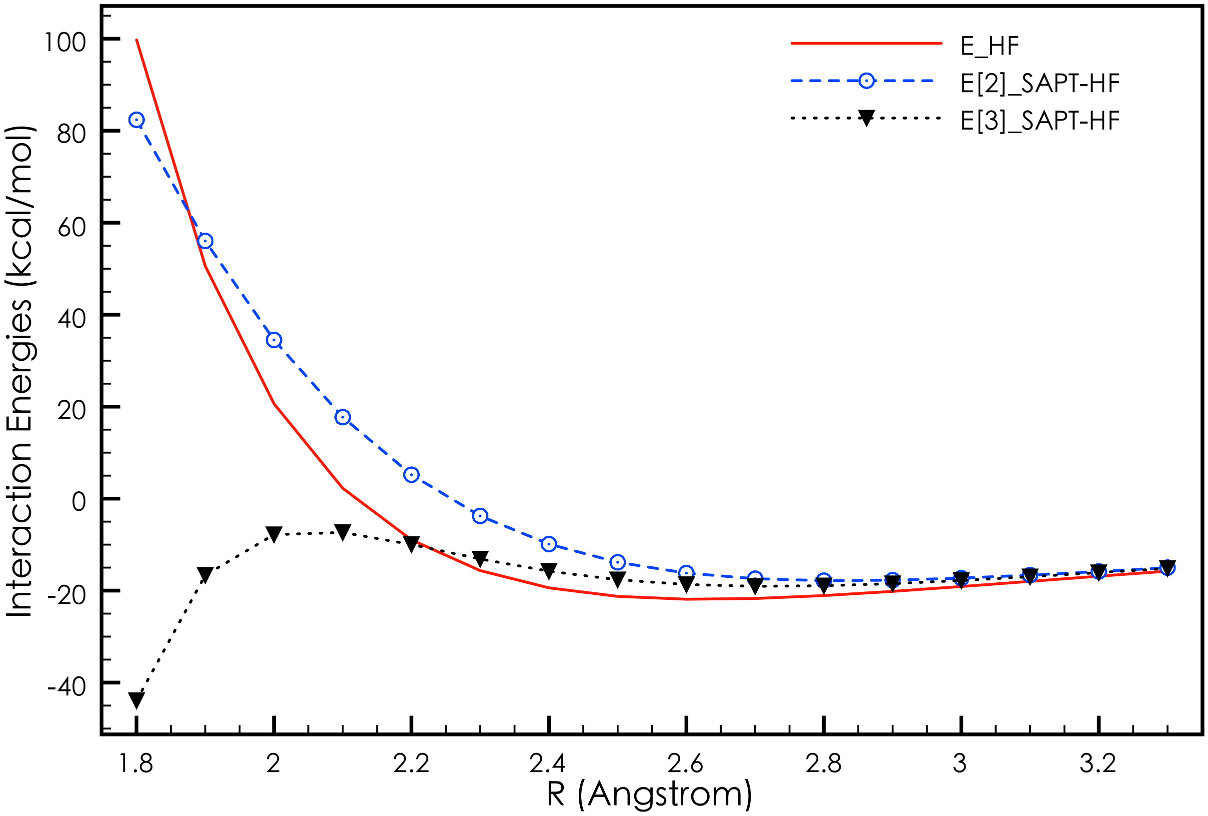

Figure S9: The supermolecular Hatree-Fock interaction energies $E_{\mathrm{int}}^{\mathrm{HF}}$ and approximate Hartree-Fock interaction energies composed by SAPT terms in second ($E_{\mathrm{SAPT-HF}}^{[2]}$) and third ($E_{\mathrm{SAPT-HF}}^{[2]}$) order for $\mathrm{OH}^- \cdots \mathrm{H_2O}$ system. R is the distance between two oxygen atoms.

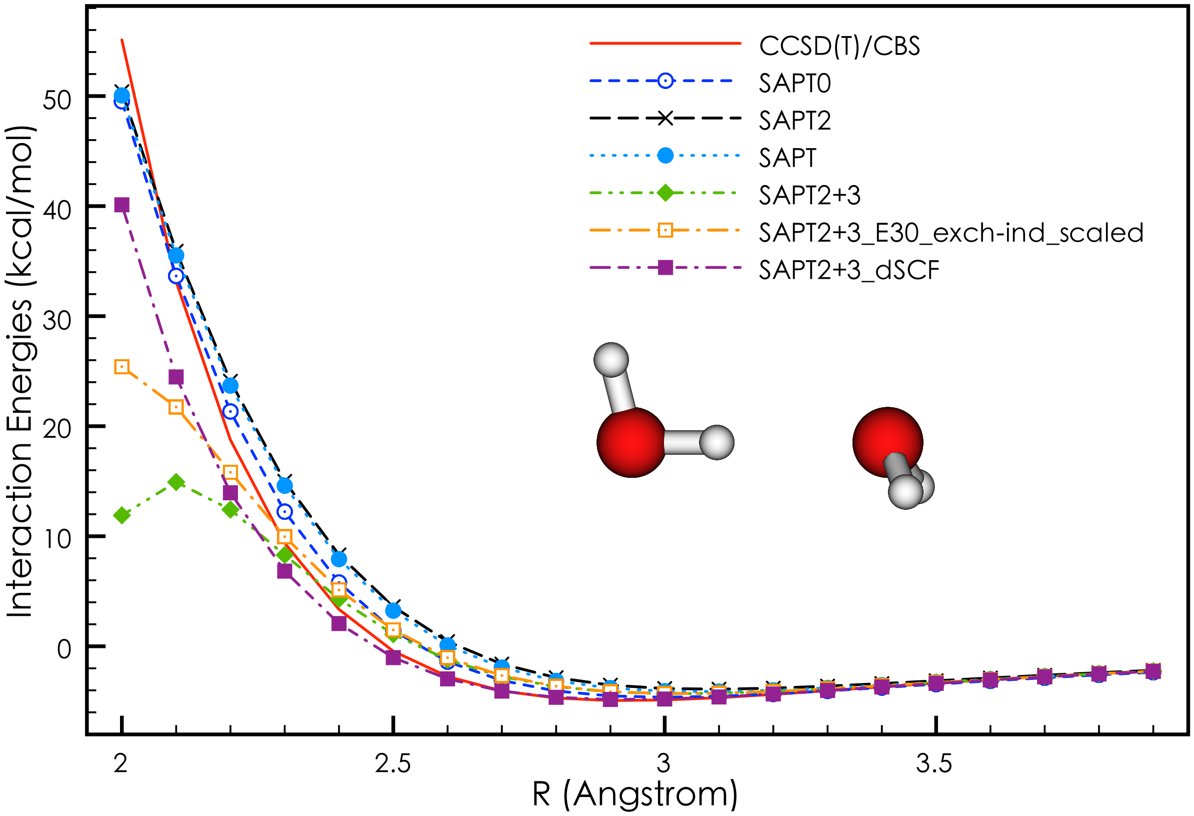

Figure S10: Comparison of performance of different levels of SAPT on the $H_2O \cdots H_2O$ system. SAPT2+3_E30_exch-ind_scaled means the interaction energies are calculated at the SAPT2+3 level with $E^{(30)}_{\mathrm{exch-ind}}$ scaled by Eq. (7). SAPT2+3_dSCF means the interaction energies are calculated at the SAPT2+3 level with $E^{(30)}_{\mathrm{ind}}$ and $E^{(30)}_{\mathrm{exch-ind}}$ substituted by $\delta E^{(2)}_{\mathrm{int}}$. R is the distance between two oxygen atoms.

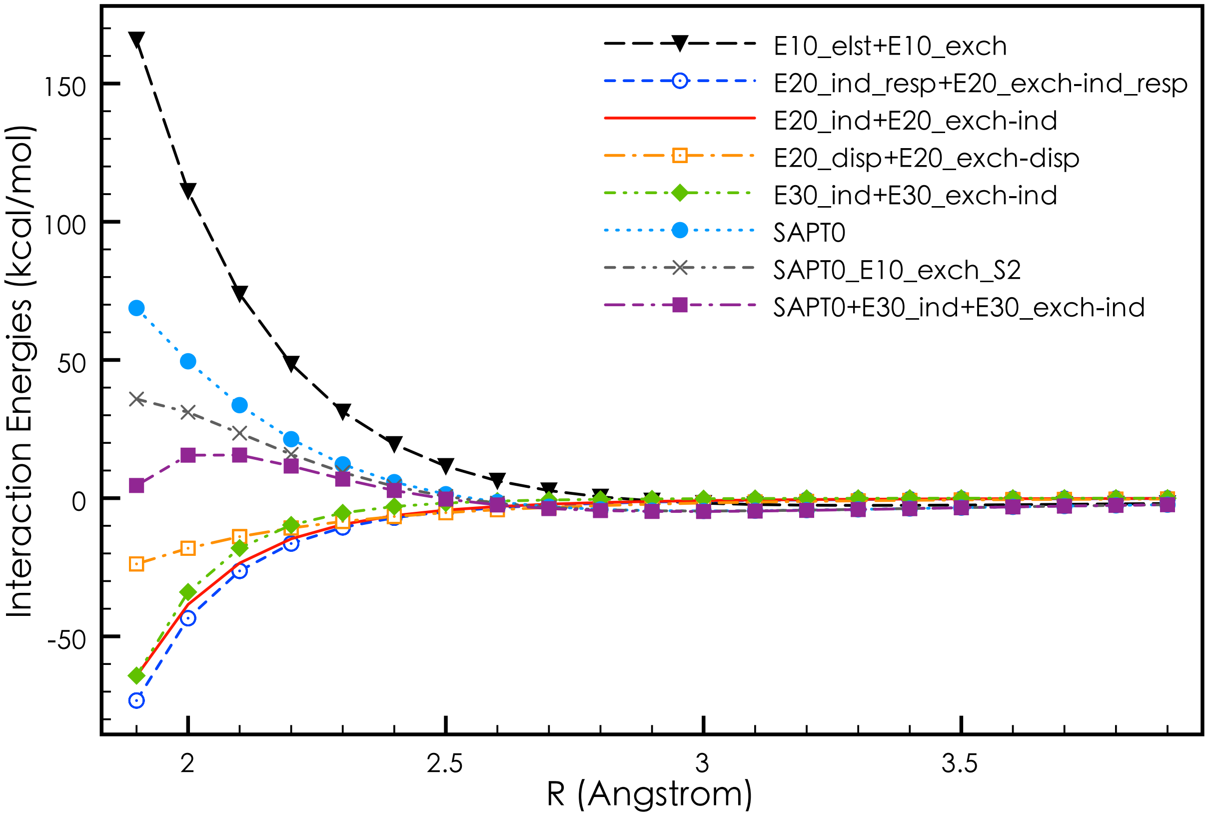

Figure S11: SAPT decomposition of the interaction energy of the $H_2O \cdots H_2O$ system into different orders of electrostatic (elst), induction (ind), and dispersion (disp) with their corresponding exchange (exch) contributions. SAPT0+E30_ind+E30_exch-ind means the interaction energies are calculated at the SAPT0 level plus $E^{(30)}_{\mathrm{ind}}$ and $E^{(30)}_{\mathrm{exch-ind}}$. R is the distance between two oxygen atoms.

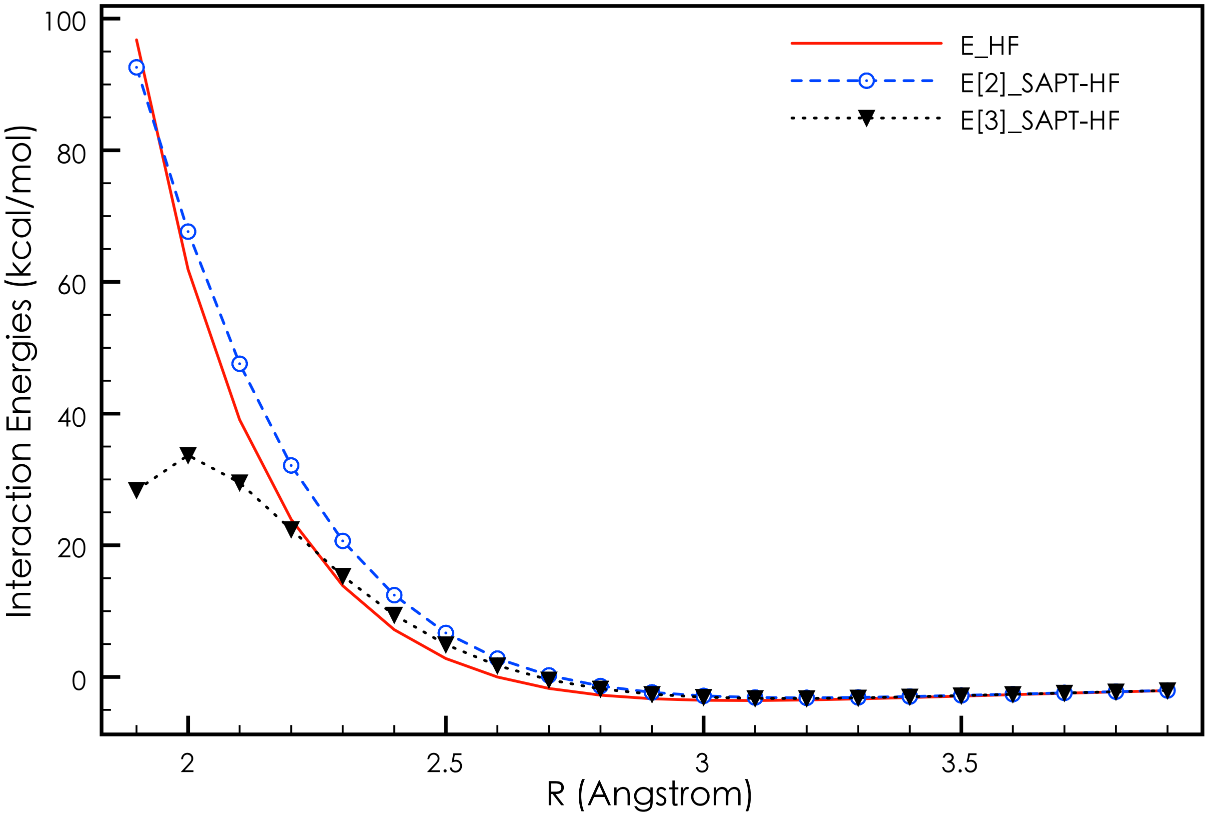

Figure S12: The supermolecular Hatree-Fock interaction energies $E^{\mathrm{HF}}_{\mathrm{int}}$ and approximate Hartree-Fock interaction energies composed by SAPT terms in second ($E^{[2]}_{\mathrm{SAPT-HF}}$) and third ($E^{[2]}_{\mathrm{SAPT-HF}}$) order for $\mathrm{H_2O} \cdots \mathrm{H_2O}$ system. R is the distance between two oxygen atoms.

References

[1] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

[2] Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Olsen, J. *Chem. Phys. Lett.* **1999**, *302*, 437.