

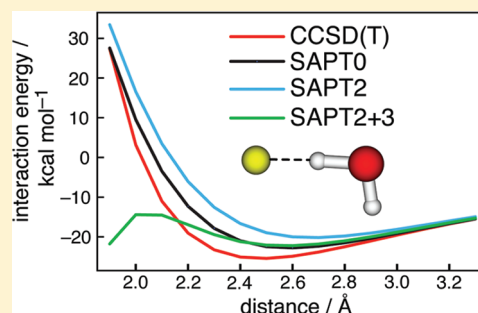
Breakdown of the Single-Exchange Approximation in Third-Order Symmetry-Adapted Perturbation Theory

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Supporting Information

ABSTRACT: We report third-order symmetry-adapted perturbation theory (SAPT) calculations for several dimers whose intermolecular interactions are dominated by induction. We demonstrate that the single-exchange approximation (SEA) employed to derive the third-order exchange–induction correction ($E_{\text{exch-ind}}^{(30)}$) fails to quench the attractive nature of the third-order induction ($E_{\text{ind}}^{(30)}$), leading to one-dimensional potential curves that become attractive rather than repulsive at short intermolecular separations. A scaling equation for $E_{\text{exch-ind}}^{(30)}$ based on an exact formula for the first-order exchange correction, is introduced to approximate exchange effects beyond the SEA, and qualitatively correct potential energy curves that include third-order induction are thereby obtained. For induction-dominated systems, our results indicate that a “hybrid” SAPT approach, in which a dimer Hartree–Fock calculation is performed in order to obtain a correction for higher-order induction, is necessary not only to obtain quantitative binding energies but also to obtain qualitatively correct potential energy surfaces. These results underscore the need to develop higher-order exchange–induction formulas that go beyond the SEA.



1. INTRODUCTION

Symmetry-adapted perturbation theory (SAPT) is a systematically improvable hierarchy of methods for direct calculation of intermolecular interaction energies,^{1–4} in which the interaction energy decomposes naturally into a sum of physically meaningful components: electrostatics, induction, dispersion, and exchange–repulsion. This is appealing because one can construct physically motivated potential energy surfaces or force fields by separately fitting the individual components of a SAPT calculation. Applications to clusters,^{5–7} molecular crystals,^{8–11} bulk liquids,¹² and biomolecules¹³ have been reported recently.

Starting from a zeroth-order Hamiltonian equal to the sum of two monomer Fock operators, the SAPT approach is based on a symmetrized Rayleigh–Schrödinger (SRS) perturbation expansion^{1,2} with respect to three perturbations: the intermolecular interaction potential, \hat{V} , and the two monomer fluctuation potentials, \hat{W}_A and \hat{W}_B . The interaction energy can be expressed as

$$E_{\text{int}} = \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} (E_{\text{pol}}^{(ij)} + E_{\text{exch}}^{(ij)}) \quad (1)$$

where i indicates the order in perturbation theory with respect to \hat{V} and j indicates the order with respect to both \hat{W}_A and \hat{W}_B . The correction terms $E_{\text{pol}}^{(ij)}$ are known collectively as the *polarization expansion*, and these are precisely the same terms that would appear in ordinary Rayleigh–Schrödinger perturbation theory. The polarization expansion contains electrostatic, induction, and dispersion interactions, but in the SRS expansion, each term $E_{\text{pol}}^{(ij)}$ has a corresponding exchange term, $E_{\text{exch}}^{(ij)}$ that

arises from the antisymmetrizer $\hat{\mathcal{A}}_{AB}$ that is introduced in order to project away the Pauli-forbidden components of the interaction energy.²

The operator $\hat{\mathcal{A}}_{AB}$ generates all possible permutations (exchanges) of electrons on monomers A and B, which makes it difficult to derive closed-form, programmable expressions for the exchange corrections. To the best of our knowledge, this has been accomplished¹⁴ only for the first-order exchange correction, $E_{\text{exch}}^{(10)}$ and all higher-order exchange terms are evaluated within the *single-exchange approximation* (SEA).¹ (Because the resulting formulas depend on the square of the dimer overlap matrix, typically denoted by S , the SEA is sometimes known as the “ S^2 approximation”.)

The SEA is thought to be quite robust at equilibrium geometries.¹⁵ As an example, we cite a recent SAPT study of dimers consisting of nonpolar monomers.¹⁶ There, the ratio $E_{\text{exch}}^{(10)}/E_{\text{exch}}^{(10)}(S^2)$, where the numerator is exact and the denominator invokes the SEA, was used as a scaling factor for the higher-order exchange terms. It was found that this scaling adds no more than 0.03 kcal/mol to binding energies at equilibrium geometries, and even at much shorter distances, where the intermolecular interaction becomes repulsive, the scaling adds no more than 1 kcal/mol. The largest contribution to this additional 1 kcal/mol comes from scaling the third-order exchange–induction term, $E_{\text{exch-ind}}^{(30)}(S^2)$.¹⁶

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A formula for the third-order exchange interaction $E_{\text{exch}}^{(30)}(S^2)$ was reported only a few years ago¹⁷ and has not yet been explored as thoroughly as have the lower-order SAPT corrections. Because $E_{\text{exch-ind}}^{(30)}$ ought to be more significant for polar molecules, as opposed to the nonpolar ones considered in ref 16, we have undertaken a careful analysis of the role of the $E_{\text{exch-ind}}^{(30)}$ term in SAPT calculations on polar dimers. The results, reported here, demonstrate that the SEA results in significant errors leading to qualitatively incorrect potential energy surfaces at distances shorter than the equilibrium intermolecular distance.

2. COMPUTATIONAL METHODS

We study potential energy curves (PECs) for five different dimers. Four of these are polar systems: $(\text{H}_2\text{O})_2$, $\text{F}^-(\text{H}_2\text{O})$, $\text{Cl}^-(\text{H}_2\text{O})$, and $\text{HO}^-(\text{H}_2\text{O})$. In addition, we consider the helium dimer as a “control experiment” because induction plays almost no role in the binding of He_2 . Third-order SAPT calculations for He_2 and $(\text{H}_2\text{O})_2$ near their equilibrium geometries have been reported previously by Patkowski et al.,^{17,18} but here, we extend these calculations to full PECs.

Rigid monomer geometries were adopted for all computations because the frozen-monomer approximation works reasonably well for PECs.^{7,8} Monomer geometries were obtained from MP2/aug-cc-pVTZ optimizations, and then, PECs were constructed along the distance coordinate, R , between the two heavy atoms. As benchmarks, we estimated the complete basis set (CBS) interaction energy at the CCSD(T) level based on a two-point (“T,Q”) extrapolation of the MP2 energy and an estimate of the triples correction in a smaller basis set. (Details can be found in the Supporting Information.) All SAPT calculations were performed in the aug-cc-pVTZ basis set using the SAPT 2008.2 program,¹⁹ with integrals generated by the ATMOL program.²⁰

The different levels of SAPT applied in this work are defined as follows⁴

$$E_{\text{SAPT0}} = E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)} \quad (2a)$$

$$E_{\text{SAPT2}} = E_{\text{SAPT0}} + E_{\text{elst,resp}}^{(12)} + E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)} + \hat{t}E_{\text{ind}}^{(22)} + \hat{t}E_{\text{exch-ind}}^{(22)} \quad (2b)$$

$$E_{\text{SAPT}} = E_{\text{SAPT2}} + E_{\text{elst,resp}}^{(13)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)} \quad (2c)$$

$$E_{\text{SAPT2+3}} = E_{\text{SAPT}} + E_{\text{ind}}^{(30)} + E_{\text{exch-ind}}^{(30)} + E_{\text{disp}}^{(30)} + E_{\text{exch-disp}}^{(30)} + E_{\text{ind-disp}}^{(30)} + E_{\text{exch-ind-disp}}^{(30)} \quad (2d)$$

The subscripts denote electrostatic (elst), exchange (exch), induction (ind), and dispersion (disp) components, and “resp” indicates that the components have been calculated including the Hartree–Fock response of each monomer to the static electric field of its interacting partner. This response, which amounts to orbital relaxation, is obtained by solving coupled-perturbed Hartree–Fock equations. The superscript “ \hat{t} ” in $\hat{t}E_{\text{ind}}^{(22)}$ indicates that this is the “true” correlation part of $E_{\text{ind}}^{(22)}$, not

included in $E_{\text{ind,resp}}^{(20)}$ and the corresponding true correlation part of $E_{\text{exch-ind}}^{(22)}$ is estimated as

$$\hat{t}E_{\text{exch-ind}}^{(22)} = \hat{t}E_{\text{ind}}^{(22)} \left(\frac{E_{\text{exch-ind,resp}}^{(20)}}{E_{\text{ind,resp}}^{(20)}} \right) \quad (3)$$

With the exception of He_2 , the dimers that we investigate are dominated by induction effects; therefore, it will be convenient to define

$$\Delta E_{\text{ind}}^{(k)} = E_{\text{ind}}^{(k0)} + E_{\text{exch-ind}}^{(k0)} \quad (4a)$$

$$\Delta E_{\text{ind,resp}}^{(k)} = E_{\text{ind,resp}}^{(k0)} + E_{\text{exch-ind,resp}}^{(k0)} \quad (4b)$$

for $k > 1$. The quantity $\Delta E_{\text{ind}}^{(k)}$ represents the contribution to the total induction energy that arises at k th order in \hat{V} , in the absence of monomer correlation,⁴ and $\Delta E_{\text{ind,resp}}^{(k)}$ is the analogous orbital-relaxed quantity.

The Hartree–Fock interaction energy, $E_{\text{int}}^{\text{HF}}$, can be approximated within SAPT, and through second- and third-order in \hat{V} , these approximations are¹⁷

$$E_{\text{SAPT-HF}}^{[2]} = E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + \Delta E_{\text{ind,resp}}^{(2)} \quad (5a)$$

$$E_{\text{SAPT-HF}}^{[3]} = E_{\text{SAPT-HF}}^{[2]} + \Delta E_{\text{ind}}^{(3)} \quad (5b)$$

Because induction interactions converge slowly for polar molecules and because one may argue that a dimer Hartree–Fock calculation contains induction and exchange–induction effects through infinite order,^{21–23} a “hybrid” SAPT approach is recommended for polar molecules.^{17,18} In this approach, a dimer Hartree–Fock calculation is used to evaluate the energy difference

$$\delta E_{\text{int}}^{(2)} = E_{\text{int}}^{\text{HF}} - E_{\text{SAPT-HF}}^{[2]} \quad (6)$$

which is then taken as an estimate of induction effects beyond second order.¹⁷ This term can then be added as a correction to any of the SAPT methods that are second-order in \hat{V} , that is, SAPT0, SAPT2, or SAPT. [Note also that what we call $\delta E_{\text{int}}^{(2)}$ has alternatively been called the $\delta E_{\text{int}}^{\text{HF}}$ correction⁴ and the $\delta(\text{HF})$ correction.²⁴] While this correction brings in higher-order induction and exchange–induction effects, it also contains spurious unphysical terms,^{14,17,23} most notably, exchange deformation of the orbitals.²³

3. RESULTS AND DISCUSSION

Qualitatively similar results are obtained for each of the four $\text{X}\cdots\text{H}_2\text{O}$ systems considered here ($\text{X} = \text{F}^-$, Cl^- , HO^- , and H_2O), and we will focus largely on $\text{F}^-(\text{H}_2\text{O})$ as an example. However, all of the quantities that we plot for $\text{F}^-(\text{H}_2\text{O})$ are plotted for each $\text{X}\cdots\text{H}_2\text{O}$ system and also for He_2 in the Supporting Information.

PECs computed for $\text{F}^-(\text{H}_2\text{O})$, using all four versions of SAPT defined in eq 2, are plotted in Figure 1. Each of these methods underbinds this dimer at near-equilibrium distances, as compared to the benchmark CCSD(T)/CBS result, but the SAPT0, SAPT, and SAPT2 curves at least exhibit reasonable shapes. However, in the case of SAPT2+3, which, in principle, is the highest-level SAPT method that is employed here, the PEC is reasonable only for $R > R_{\text{eq}}$, where R_{eq} denotes the minimum-energy intermolecular distance computed at the CCSD(T)/CBS level. [For $\text{F}^-(\text{H}_2\text{O})$, $R_{\text{eq}} = 2.5 \text{ \AA}$.] At shorter

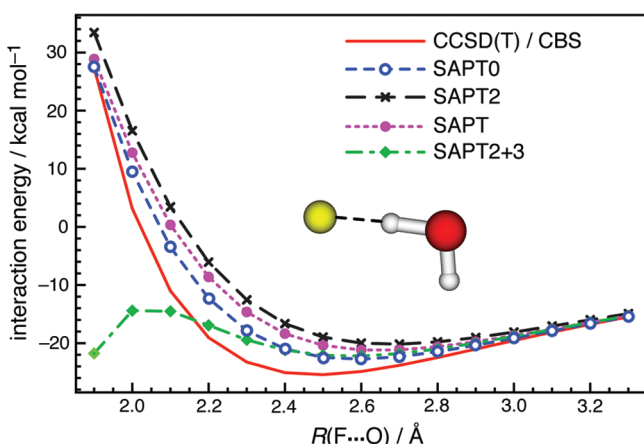


Figure 1. Comparison of different levels of SAPT (as defined in eq 2) for the $F^-(H_2O)$ system. The H_2O geometry is frozen in these potential energy scans.

distances, the SAPT2+3 curve turns over, becoming attractive rather than repulsive.

The reason for this failure can be discerned by decomposing the interaction energy into different components, some of which are plotted in Figure 2. Attractive interactions in $F^-(H_2O)$ are

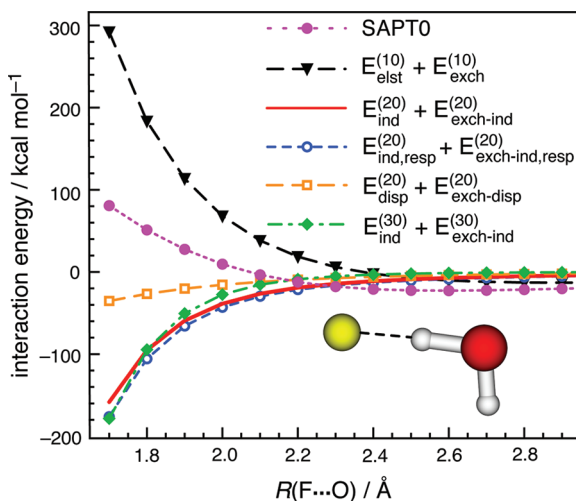


Figure 2. SAPT0 decomposition of the interaction energy for $F^-(H_2O)$ into different orders of electrostatic (elst), induction (ind), and dispersion (disp) components, each with a corresponding exchange (exch) contribution. For the second-order induction and exchange–induction components, results are shown both with and without orbital relaxation (resp) corrections.

dominated by induction, and we observe that for $R < 1.8 \text{ \AA}$, the third-order induction correction, $\Delta E_{\text{ind}}^{(3)}$, is even larger than $\Delta E_{\text{ind}}^{(2)}$. Although a variety of third-order terms are present in a SAPT2+3 calculation (see eq 2d), if we add $\Delta E_{\text{ind}}^{(3)}$ to an otherwise qualitatively correct SAPT0 calculation, the result is a PEC that is completely wrong at short R . This result is shown in Figure 3 for all four ion–water complexes considered here. These calculations identify $\Delta E_{\text{ind}}^{(3)}$ as the origin of the problem.

In Figure 4, we address the convergence of the SAPT approximations to the supermolecular Hartree–Fock interaction energy for $F^-(H_2O)$ and also for $(H_2O)_2$. For either system, both $E_{\text{SAPT-HF}}^{(2)}$ and $E_{\text{SAPT-HF}}^{(3)}$ are excellent approximations to $E_{\text{int}}^{\text{HF}}$ for $R \geq R_{\text{eq}}$. For intermolecular distances a bit shorter than

R_{eq} , the addition of $\Delta E_{\text{ind}}^{(3)}$ to $E_{\text{SAPT-HF}}^{(2)}$ (which defines the third-order approximation, $E_{\text{SAPT-HF}}^{(3)}$) successfully accounts for the difference between $E_{\text{int}}^{\text{HF}}$ and $E_{\text{SAPT-HF}}^{(2)}$. Thus, the third-order approximation to $E_{\text{int}}^{\text{HF}}$ is basically converged for distances ranging from a bit shorter than R_{eq} out to $R = \infty$. For $(H_2O)_2$ near its equilibrium geometry, this convergence was noted previously by Patkowski et al.,^{17,18} but even for the anion–water systems considered here, where the induction effects are larger, we find that $E_{\text{SAPT-HF}}^{(3)}$ is an excellent approximation to $E_{\text{int}}^{\text{HF}}$ near the equilibrium geometry and also at larger values of R .

In contrast, for $R \ll R_{\text{eq}}$, the second-order approximation $E_{\text{SAPT-HF}}^{(2)}$ is clearly *not* converged for $F^-(H_2O)$, although the PEC defined by the $E_{\text{SAPT-HF}}^{(2)}$ method is at least qualitatively correct. For $(H_2O)_2$, where the binding energy and the induction effects are much smaller, $E_{\text{SAPT-HF}}^{(2)}$ is a much better approximation to the Hartree–Fock interaction energy. For both systems, addition of $\Delta E_{\text{ind}}^{(3)}$ to $E_{\text{SAPT-HF}}^{(2)}$, which defines the third-order approximation $E_{\text{SAPT-HF}}^{(3)}$, improves upon $E_{\text{SAPT-HF}}^{(2)}$ at distances somewhat shorter than R_{eq} , but eventually, the $E_{\text{SAPT-HF}}^{(3)}$ curves turn over, even in the charge-neutral water dimer. This behavior is clearly a manifestation of the divergence of $\Delta E_{\text{ind}}^{(3)}$ at short intermolecular separation, which again points to this quantity as the culprit responsible for the qualitatively wrong PECs obtained at the SAPT2+3 level of theory.

One might object that in our calculations, the third-order induction terms do not include orbital relaxation (response) effects. At near-equilibrium geometries, Patkowski et al.¹⁸ have shown that orbital relaxation increases the third-order induction interaction by up to 50% for dimers such as $(H_2O)_2$ that are composed of polar monomers. Anion–water complexes were not considered by Patkowski et al., but for $F^-(H_2O)$, the second-order induction corrections are compared, with and without orbital relaxation, in Figure 2. The effect of orbital relaxation is to make the potential energy curve more attractive at short distances, albeit by a relatively small amount. As such, we find it unlikely that the inclusion of orbital response at third order would correct the qualitatively wrong PECs caused by $\Delta E_{\text{ind}}^{(3)}$.

Thus, the question remains, what is the problem with the $\Delta E_{\text{ind}}^{(3)}$ term? According to Figure 2, the interaction energy contributed by $\Delta E_{\text{ind}}^{(3)}$ increases as the intermolecular distance decreases; therefore, it must be that $E_{\text{ind}}^{(30)}$ is not sufficiently quenched by its exchange counterpart, $E_{\text{exch-ind}}^{(30)}$, at short distance. The $\Delta E_{\text{ind}}^{(2)}$ (or $\Delta E_{\text{ind,resp}}^{(2)}$) curve has roughly the same basic shape as that for $\Delta E_{\text{ind}}^{(3)}$, although the latter diverges slightly more rapidly than the former as R decreases; it is difficult to ascribe any qualitative problems to this subtle difference.

Perhaps more telling are certain calculations reported in Figure 3, in which we have replaced the exact $E_{\text{exch}}^{(10)}$ term in a SAPT0 calculation with its SEA, $E_{\text{exch}}^{(10)}(S^2)$. For each of the four $X \cdots H_2O$ systems that we consider (including the water dimer), this has the effect of greatly weakening the short-range repulsive interactions, and for $F^-(H_2O)$ and $HO^-(H_2O)$, where induction effects are largest, this modified SAPT0 potential curve even becomes attractive at sufficiently short distance. Therefore, even at first order, the SEA can produce attractive PECs at short distances, although the influence of the SEA on the third-order corrections is much larger. One might expect that the SEA might also have qualitatively important effects on the *second*-order exchange at short intermolecular distances, but in fact, qualitatively correct PECs are obtained using SAPT methods that are only second-order in \hat{V} .

For the $X \cdots H_2O$ systems, the value of the turnover point where the SAPT0 + $\Delta E_{\text{ind}}^{(30)}$ potential curve (Figure 3) changes

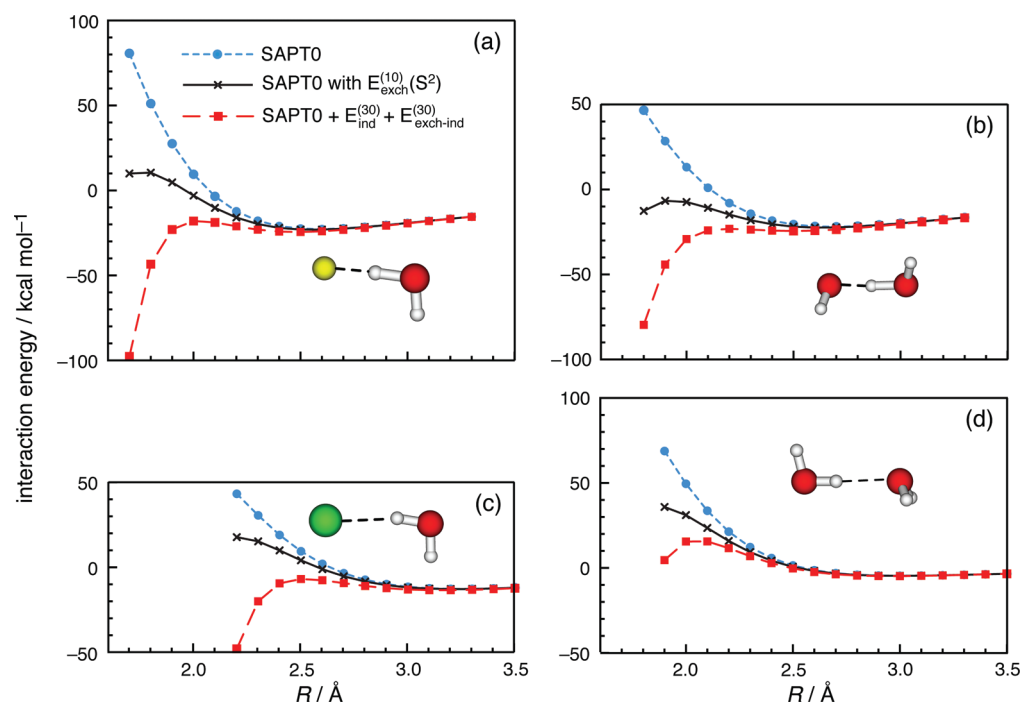


Figure 3. SAPTO potential curves for (a) $F^- \cdots H_2O$, (b) $HO^- \cdots H_2O$, (c) $Cl^- \cdots H_2O$, and (d) $H_2O \cdots H_2O$ as a function of the distance R between the two heavy atoms. (Both the vertical and horizontal scales are the same in all four panels.) Also shown are the potential curves that result when $\Delta E_{ind}^{(3)}$ is added to a SAPTO calculation and when the exact $E_{exch}^{(10)}$ term in SAPTO is replaced by its single-exchange approximation, $E_{exch}^{(10)}(S^2)$. Results for the helium dimer are not shown because all three curves are indistinguishable on the energy scale used in this figure.

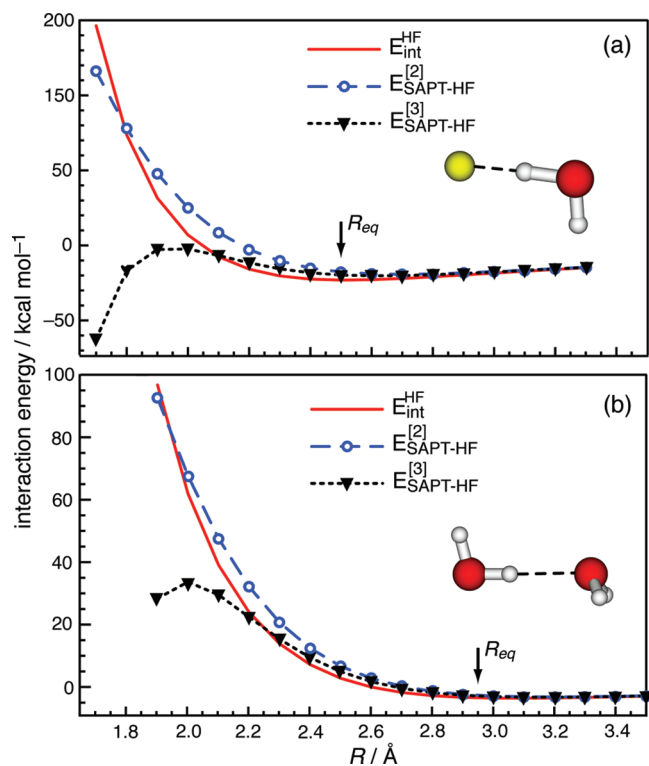


Figure 4. Distance dependence of the supermolecular Hartree-Fock interaction energy (E_{int}^{HF}) and its second-order ($E_{SAPT-HF}^{[2]}$) and third-order ($E_{SAPT-HF}^{[3]}$) SAPT approximations for (a) $F^-(H_2O)$ and (b) $(H_2O)_2$. In each case, the coordinate R is the distance between the heavy atoms, and the arrow indicates the CCSD(T)/CBS minimum-energy geometry. Note that the two panels use different energy scales.

from repulsive to attractive decreases in the order $Cl^- > HO^- > H_2O > F^-$. (The turnover points for SAPT2+3 calculations occur in the same order; see Table 1.) For the anions, this is the

Table 1. CCSD(T)/CBS Equilibrium Distances and SAPT2+3 “Turnover Points” Where the Potential Becomes Attractive at Short Distance

system	$R_{eq}/\text{\AA}$	turnover point/ \AA
$F^-(H_2O)$	2.5	1.9
$HO^-(H_2O)$	2.6	2.1
$Cl^-(H_2O)$	3.1	2.4
$(H_2O)_2$	2.9	2.0

same as the order of the ionic radii ($Cl^- > O^{2-} > F^-$), which we rationalize in terms of the fact that ions with larger radii would be expected to have larger exchange–repulsion interactions, at least for intermolecular distances not significantly smaller than the sum of the van der Waals radii. Considering the water dimer, the aforementioned turning point occurs at a smaller value of R than it does in $HO^-(H_2O)$, which we attribute to the much larger induction effects in the ionic complex. Together, these observations suggest that the large negative values of $\Delta E_{ind}^{(3)}$ at small R are probably attributable to the failure of $E_{exch-ind}^{(30)}(S^2)$ to quench $E_{ind}^{(30)}$.

Following ref 16, we use the ratio $E_{exch}^{(10)}/E_{exch}^{(10)}(S^2)$ to estimate third-order exchange effects beyond the SEA. Thus, we introduce an *ad hoc* scaling formula

$$E_{exch-ind, scale}^{(30)} = E_{exch-ind}^{(30)} \left(\frac{E_{exch}^{(10)}}{E_{exch}^{(10)}(S^2)} \right)^\alpha \quad (7)$$

where the exponent α is an empirical parameter. (In ref 16, only $\alpha = 1$ was considered.) Figure 5 shows the result when

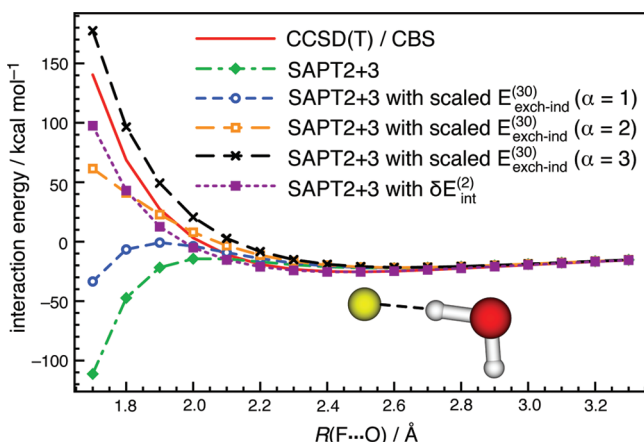


Figure 5. Comparison of several variants of SAPT2+3 for $\text{F}^-(\text{H}_2\text{O})$. In three of these variants, the second- or third-order exchange–induction term has been scaled using eq 7 with different values of the parameter α . In another variant, we have replaced the $\Delta E_{\text{ind}}^{(3)}$ term in SAPT2+3 with the $\delta E_{\text{int}}^{(2)}$ correction defined in eq 6 in order to capture higher-order induction effects.

$E_{\text{exch-ind}}^{(30)}$ is replaced in a SAPT2+3 calculation by the scaled version in eq 7. This replacement has little effect for $R \geq R_{\text{eq}}$, which is an indication of the robustness of the SEA at equilibrium geometries and beyond. At short intermolecular distances, however, scaling using $\alpha = 3$ corrects the qualitatively incorrect SAPT2+3 potential curves. The choice $\alpha = 2$ also prevents the PEC from turning over at short distance, although the shape of the repulsive wall is not correct, and with $\alpha = 1$, the PEC still turns over at short distance. There is no sound theoretical justification for any choice of α , but the fact that $\alpha > 1$ is required to obtain a qualitatively correct PEC indicates that exchange interactions beyond the SEA are more important at third order than they are at first order when the intermolecular distance is small.

On the other hand, a SAPT2+3 calculation where $\Delta E_{\text{ind}}^{(3)}$ is replaced by $\delta E_{\text{int}}^{(2)}$ is in quantitative agreement with CCSD(T)/CBS results for $R \geq R_{\text{eq}}$ (see Figure 5). While this SAPT2+3 + $\delta E_{\text{HF}}^{(2)}$ result is not quantitative for $R < R_{\text{eq}}$ (which is to be expected, owing to the spurious exchange contributions present in $\delta E_{\text{int}}^{(2)}$), at the very least, this curve does not turn over at small R and remains qualitatively correct even at very short intermolecular separations. In the strongly repulsive region of the PEC, the SAPT2+3 + $\delta E_{\text{HF}}^{(2)}$ result is superior to the PEC obtained simply by scaling $E_{\text{exch-ind}}^{(30)}$ using $\alpha = 1$ or 2.

Actually, SAPT methods that are only second order in \hat{V} also suffer from the effects of SEA. Although these methods are free of the disastrous turnover of the PEC that SAPT2+3 exhibits, the PECs are less accurate at short distances. We use the SAPT0 method as an example to illustrate the effects of SEA on the second-order exchange (SAPT and SAPT2 afford similar results) and thus define another scaling formula

$$E_{\text{exch-ind,resp}}^{(20)} = E_{\text{exch-ind,resp}}^{(20)} \left(\frac{E_{\text{exch}}^{(10)}}{E_{\text{exch}}^{(10)}(S^2)} \right)^\alpha \quad (8)$$

The exponent α is once again an empirical parameter. Figure 6 shows the result when $E_{\text{exch-ind,resp}}^{(20)}$ is replaced in a SAPT0 calculation by the scaled version in eq 8. All of the PECs are

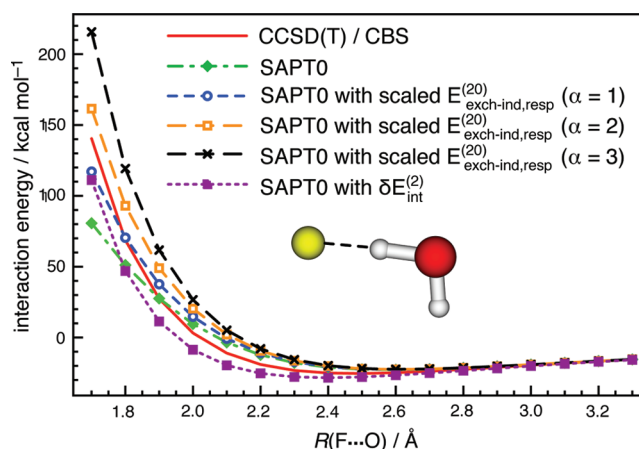


Figure 6. Comparison of several variants of SAPT0 for $\text{F}^-(\text{H}_2\text{O})$. In three of these, the $E_{\text{exch-ind,resp}}^{(20)}$ term has been scaled using eq 8, with different values of the parameter α , in order to approximate exchange interactions beyond the SEA. In another, we have added the $\delta E_{\text{int}}^{(2)}$ correction defined in eq 6 to SAPT0 in order to capture higher-order induction effects.

reasonable, although the unscaled SAPT0 PEC starts to flatten out at very short distance ($R < 1.8$ Å). Scaling with $\alpha = 1$ or 2 corrects this defect and affords fairly accurate PECs, whereas the choice $\alpha = 3$ (which was required in order to correct the flattening out or turning over of the SAPT2+3 PECs) overcorrects the SAPT0 results. At the SAPT0 level, $\alpha = 3$ is less accurate as compared to smaller values of α , which affirms our conclusion that the effect of the SEA on the third-order exchange is much more significant than it is at second order.

Addition of the $\delta E_{\text{int}}^{(2)}$ correction improves both the SAPT0 and SAPT2+3 results at short intermolecular distances (see Figures 5 and 6, respectively). This is consistent with previous recommendations to use the $\delta E_{\text{int}}^{(2)}$ correction term when the monomers are polar.^{17,18} (For nonpolar monomers, the unphysical artifacts inherent to this correction are more significant, relative to the very small induction corrections, and better results are sometimes obtained *without* using this correction.¹⁷) However, the recommendation to use $\delta E_{\text{int}}^{(2)}$ is based on benchmark calculations for systems such as $(\text{H}_2\text{O})_2$ at its equilibrium geometry.¹⁷ For $\text{F}^-(\text{H}_2\text{O})$, it is not clear that addition of $\delta E_{\text{int}}^{(2)}$ to a SAPT0 calculation actually improves the results. This is difficult to see on the scale plotted in Figure 6; therefore, an enlarged view is shown in Figure 7.

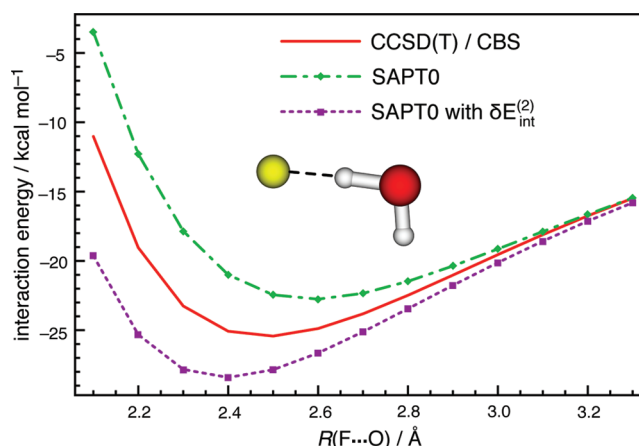


Figure 7. Comparison of SAPT0 for $\text{F}^-(\text{H}_2\text{O})$ with and without the $\delta E_{\text{int}}^{(2)}$ correction defined in eq 6.

4. CONCLUSIONS

We have found that the $E_{\text{exch-ind}}^{(30)}$ term in SAPT, which at present can be computed only within the single-exchange approximation, fails to quench $E_{\text{ind}}^{(30)}$ at short intermolecular distances. This leads to the anomalous result that potential energy curves for polar systems become *attractive* at sufficiently small intermolecular distances. For the three anion–water complexes considered here, “sufficiently small” means about 0.5 Å shorter than the equilibrium monomer separation, while for $(\text{H}_2\text{O})_2$, the turnover occurs at $R = 2.0$ Å as compared to $R_{\text{eq}} = 2.9$ Å. Scaling $E_{\text{exch-ind}}^{(30)}$ based on the ratio $E_{\text{exch}}^{(10)}/E_{\text{exch}}^{(10)}(S^2)$ approximates some higher-order exchange effects sufficiently well to avoid catastrophic divergence of the potential energy curve, but for highly polar systems, this result serves mostly to identify the nature of the problem rather than to correct it. Further amplification of this ratio, that is, using $[E_{\text{exch}}^{(10)}/E_{\text{exch}}^{(10)}(S^2)]^\alpha$ for $\alpha \approx 3$, is required in order to obtain potential energy curves that are qualitatively correct at short distances. Alternatively, calculation of the $\delta E_{\text{int}}^{(2)}$ correction cannot be avoided, even at third order, if full potential energy curves are required.

Interestingly, even in cases where the third-order method fails catastrophically, *second-order* SAPT potential curves remain qualitatively correct even at rather small intermolecular distances. This suggests that the single-exchange approximation is more severe in the case of $E_{\text{exch-ind}}^{(30)}$ than it is for lower-order exchange interactions, at least for highly polar monomers. This points to the importance of developing post-SEA correction formulas at higher orders in SAPT. Furthermore, our results show that it is inadvisable to include $E_{\text{ind}}^{(30)}$ and $E_{\text{exch-ind}}^{(30)}$ when constructing analytic potential energy surfaces based on SAPT.

■ ASSOCIATED CONTENT

Supporting Information

Additional computational details and potential energy curves for $\text{Cl}^-(\text{H}_2\text{O})$, $\text{HO}^-(\text{H}_2\text{O})$, $(\text{H}_2\text{O})_2$, and He_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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