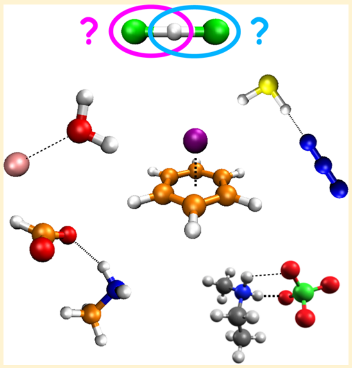
JCTC Journal of Chemical Theory and Computation
Article
pubs.acs.org/JCTC

Accurate Description of Intermolecular Interactions Involving Ions Using Symmetry-Adapted Perturbation Theory

Ka Un Lao,[†] Rainer Schäffer,[‡] Georg Jansen,*[,‡] and John M. Herbert*[,†]

[†]Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States
[‡]Fakultät für Chemie, Universität Duisburg-Essen, 45117 Essen, Germany

Ⓢ *Supporting Information*



ABSTRACT: Three new data sets for intermolecular interactions, AHB21 for anion–neutral dimers, CHB6 for cation–neutral dimers, and IL16 for ion pairs, are assembled here, with complete-basis CCSD(T) results for each. These benchmarks are then used to evaluate the accuracy of the single-exchange approximation that is used for exchange energies in symmetry-adapted perturbation theory (SAPT), and the accuracy of SAPT based on wave function and density-functional descriptions of the monomers is evaluated. High-level SAPT calculations afford poor results for these data sets, and this includes the recently proposed "gold", "silver", and "bronze standards" of SAPT, namely, SAPT2+(3)-δMP2/aug-cc-pVTZ, SAPT2+/aug-cc-pVDZ, and sSAPT0/jun-cc-pVDZ, respectively [Parker, T. M., et al., *J. Chem. Phys.* **2014**, *140*, 094106]. Especially poor results are obtained for symmetric shared-proton systems of the form $X^{-}\cdots H^{+}\cdots X^{-}$, for X = F, Cl, or OH. For the anionic data set, the SAPT2+(CCD)-δMP2/aug-cc-pVTZ method exhibits the best performance, with a mean absolute error (MAE) of 0.3 kcal/mol and a maximum error of 0.7 kcal/mol. For the cationic data set, the highest-level SAPT method, SAPT2+3-δMP2/aug-cc-pVQZ, outperforms the rest of the SAPT methods, with a MAE of 0.2 kcal/mol and a maximum error of 0.4 kcal/mol. For the ion-pair data set, the SAPT2+3-δMP2/aug-cc-pVTZ performs the best among all SAPT methods with a MAE of 0.3 kcal/mol and a maximum error of 0.9 kcal/mol. Overall, SAPT2+3-δMP2/aug-cc-pVTZ affords a small and balanced MAE (<0.5 kcal/mol) for all three data sets, with an overall MAE of 0.4 kcal/mol. Despite the breakdown of perturbation theory for ionic systems at short-range, SAPT can still be saved given two corrections: a "δHF" correction, which requires a supermolecular Hartree–Fock calculation to incorporate polarization effects beyond second order, and a "δMP2" correction, which requires a supermolecular MP2 calculation to account for higher-order induction-dispersion coupling. These corrections serve to remove artifacts introduced by the single exchange approximation in the exchange–induction and exchange–dispersion interactions, and obviate the need for *ad hoc* scaling of the first- and second-order exchange energies. Finally, some density-functional and MP2-based electronic structure methods are assessed as well, and we find that the best density-functional method for computing binding energies in these data sets is B97M-V/aug-cc-pVTZ, which affords a MAE of 0.4 kcal/mol, whereas complete-basis MP2 affords an MAE of 0.3 kcal/mol.

I. INTRODUCTION

Noncovalent interactions play an important role in a broad range of chemical systems, from the aggregation of rare gases to the formation of crystal structures.[1−3] The coupled-cluster singles and doubles method with perturbative triples, CCSD(T), evaluated in the complete-basis limit, is still considered to be the gold standard for noncovalent interaction energies, as higher-order electron correlation effects typically contribute ≪0.1 kcal/mol.[4,5] However, the computational scaling of CCSD(T) is $\mathcal{O}(N^7)$ with respect to total system size, N, which renders this approach unfeasible for large systems. Density functional theory (DFT), however, can routinely be applied to systems with more than 1,000 basis functions on ordinary workstations, but most conventional functionals fail to account for the long-range part of the dispersion interaction.

There are several strategies to address this issue, including brute-force parametrization (as in the Minnesota density functionals[6]) as well as the addition of explicit, classical C_6/R^6 atom–atom dispersion potentials, as in the "DFT-D" approach popularized by Grimme and co-workers.[7] Nonlocal correlation functionals have also been developed to address this issue.[8−12]

Unlike these *supermolecular* methods, symmetry-adapted perturbation theory (SAPT) offers a way to compute intermolecular interactions in a physically meaningful way, as a sum of electrostatic, induction, and dispersion interactions along with their exchange counterparts.[13−18] Importantly, zeroth-order basis set superposition error (BSSE) is absent in SAPT calculations. SAPT methods traditionally use the Hartree–Fock (HF) determinants for the monomers as reference wave functions (HF-SAPT) and a double perturbation expansion to account for both *inter*molecular interactions (between monomers) as well as *intra*molecular electron correlation. The latter is treated as in Møller–Plesset perturbation theory[13,19] or coupled-cluster theory,[20−24] and together, this double-perturbation expansion constitutes a successful approach to determining intermolecular

Received: November 26, 2014
Published: April 17, 2015

DOI: 10.1021/ct5010593
J. Chem. Theory Comput. 2015, 11, 2473–2486

interactions, with results that compare favorably to complete-basis CCSD(T) calculations for dimers of neutral molecules.[13−17] The computational cost is high, though considerable progress has been made recently in reducing the computational cost,[25−27] and systems as large as a DNA intercalation complex have been treated in this way.[28] Alternatively, SAPT based on a DFT description of monomers has been used, in an approach known either as DFT-SAPT or SAPT(DFT).[18,29,30] In this case, asymptotic correction of the monomer exchange-correlation potentials is necessary in order to obtain accurate energy components.[31−33]

High-order SAPT methods exhibit good quantitative accuracy for describing intermolecular interactions between *neutral* monomers,[17] and while these methods have sometimes been applied to ionic systems as well,[34−43] these studies have mostly focused on qualitative trends.[35,36,39] Where ionic monomers are involved, the perturbation theory is typically slowly convergent and possibly even divergent,[38] and "chemical accuracy" (error $\lesssim$1 kcal/mol) may not be realized in such cases.

There have been only a few attempts to benchmark SAPT for ionic systems. These include a study by Matczak,[40] who investigated 16 pairs of alkali halides (A^+X^-) whose binding energies exceed 100 kcal/mol. That study concluded that the wave function-based SAPT method is superior to CCSD(T) in the same basis set, which in our opinion is probably a manifestation of the fact that SAPT calculations are largely free of BSSE since the CCSD(T) results were not extrapolated to the basis-set limit. In any case, neither SAPT nor CCSD(T) achieves chemical accuracy, as compared to experiment, for these alkali halides.[40] However, Ansorg et al.[41] studied the cation-π interaction between NH_4^+ and benzene using DFT-SAPT, and demonstrated good agreement between CCSD(T) and DFT-SAPT with a triple-ζ basis set. Two of us[44,45] have recently examined $HeCl^-$, $NeNa^+$, and Li^+F^-, with an eye toward understanding the role of the single-exchange approximation in describing the repulsive wall, while Korona[42] has performed DFT-SAPT calculations on $F^-(HF)$, $F^-(H_2O)$, and $Na^+(H_2O)$, finding good agreement with SAPT-(CCSD) energy components.

The aforementioned studies are insufficient to determine the complete-basis CCSD(T) result or to evaluate whether SAPT can describe intermolecular interactions in ionic systems in a general way. The aim of this work is, first, to establish complete-basis CCSD(T) benchmarks for a broad range of cationic, anionic, and ion-pair systems. Then, these benchmark values will be used to compare various levels of wave function-based SAPT, along with the recently developed "attenuated" MP2 method that has been suggested for noncovalent interactions.[46−49] Finally, DFT-SAPT and several supermolecular density functionals will be tested for the same data set, including some relatively new functionals that have been suggested to be accurate for noncovalent interactions. Lao and Herbert[50,51] have recently shown that a number of density functionals that had previously been recommended for noncovalent interactions yield poor results for binding energies of halide anions in water clusters, and the more extensive tests reported here confirm that binding energies in ionic systems are challenging tests for DFT.

II. METHODS

A. Symmetry-Adapted Perturbation Theory. The SAPT interaction energy can be expressed as[14]

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

where i indicates the order in perturbation theory with respect to the intermolecular potential, and j indicates the order with respect to the intramolecular electron correlation (the "fluctuation potential", in the language of Møller−Plesset perturbation theory). The terms $E_{\text{pol}}^{(ij)}$ originate from the so-called polarization expansion and contain electrostatic, induction, and dispersion interactions. Each term $E_{\text{pol}}^{(ij)}$ has a corresponding exchange term, $E_{\text{exch}}^{(ij)}$, that arises from antisymmetry requirements.

The simplest SAPT method, often called SAPT0, neglects intramolecular electron correlation and treats the intermolecular perturbation up to second order:

$$\begin{aligned} E_{\text{int}}^{\text{SAPT0}} &= [E_{\text{elst}}^{(10)}]_{\text{elst}} + [E_{\text{exch}}^{(10)}]_{\text{exch}} \\ &\quad + [E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + \delta E_{\text{HF}}^{(2)}]_{\text{ind}} \\ &\quad + [E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)}]_{\text{disp}} \end{aligned} \tag{2}$$

Following ref 43, the various terms in the SAPT0 energy expression are grouped, using square brackets, into electrostatic, exchange, induction, and dispersion interactions, according to the partitioning scheme used by Sherrill et al.[17,43] The Hartree−Fock correction term (δHF) up to second order, $\delta E_{\text{HF}}^{(2)}$, incorporates polarization effects beyond second order and is defined as

$$\begin{aligned} \delta E_{\text{HF}}^{(2)} &= E_{\text{int}}^{\text{HF}} - E_{\text{elst}}^{(10)} - E_{\text{exch}}^{(10)} \\ &\quad - E_{\text{ind,resp}}^{(20)} - E_{\text{exch-ind,resp}}^{(20)} \end{aligned} \tag{3}$$

where $E_{\text{HF}}^{\text{int}}$ is the counterpoise-corrected HF binding energy for the dimer. The "response" ("resp") subscripts indicate that the response correction for induction is incorporated by solving coupled-perturbed HF equations.[52,53]

Traditionally, a closed-form analytic formula for the SAPT exchange energies has been available only at first order ($E_{\text{exch}}^{(10)}$), whereas higher-order exchange terms have been evaluated using the "single-exchange approximation" (SEA). Formulas obtained from the SEA involve the square of the orbital overlap matrix ($\mathbf{S}^2$); hence, this is also known as the "S^2 approximation".[13] Schäffer and Jansen[44,45] have recently extended the complete derivation to second order, i.e., they have derived $E_{\text{exch}}^{(20)}$ without invoking the SEA, and results using exact second-order exchange will be examined here.

Lao and Herbert[38] have previously shown that use of the SEA in third-order exchange-induction, $E_{\text{exch-ind}}^{(30)}$, breaks down severely for ionic systems at short intermolecular distances. Following refs 54 and 55, we introduced an *ad hoc* scaling factor that is then used to scale $E_{\text{exch-ind,resp}}^{(20)}$ and $E_{\text{exch-ind,resp}}^{(30)}$ for correcting the deficiency of SEA:

$$p_{\text{ex}}(\alpha) = \left(\frac{E_{\text{exch}}^{(10)}}{E_{\text{exch}}^{(10)}(S^2)} \right)^{\alpha} \tag{4}$$

In eq 4, the numerator represents the exact first-order exchange energy, while the denominator is evaluated within the SEA. The idea is to use the ratio between exact and S^2 first-order exchange energies as a means to estimate the error in the SEA used in the second-order exchange-induction energies, although Schäffer and Jansen have suggested the difference is smaller at first order than at second order.[44,45] In a recent study of $F^-(H_2O)$,[38] we used the exponent $\alpha = 2$ for $E_{\text{exch-ind,resp}}^{(20)}$ and $\alpha = 3$ for $E_{\text{exch-ind,resp}}^{(30)}$, the latter value having been recommended for strongly hydrogen-bonded systems where the intermolecular

DOI: 10.1021/ct5010593
J. Chem. Theory Comput. 2015, 11, 2473−2486

distances are small, and thus, the exchange energies are large.[43] The value value $\alpha = 1$ has been used in other studies,[43,55] and some results with $\alpha = 1$ are presented here as well.

In previous work, Lao and Herbert[38] demonstrated that the $\delta E_{\mathrm{HF}}^{(2)}$ correction improves the SAPT results for $\mathrm{F^-(H_2O)}$ at short intermolecular distances, consistent with previous recommendations that the $\delta E_{\mathrm{HF}}^{(2)}$ correction is important for dimers composed of polar monomers.[56,57] The $\delta E_{\mathrm{HF}}^{(2)}$ term cancels the $p_{\mathrm{ex}}(\alpha)$ scaling correction for $E_{\text{exch-ind,resp}}^{(20)}$, and the errors in $E_{\text{exch-ind,resp}}^{(20)}$ arising from the SEA can thus be avoided. On the basis of the $p_{\mathrm{ex}}(\alpha)$ scaling factor, Parker et al.[43] proposed a "scaled" SAPT0 method, *s*SAPT0:

$$\begin{aligned} E_{\mathrm{int}}^{s\mathrm{SAPT0}} &= [E_{\mathrm{elst}}^{(10)}]_{\mathrm{elst}} + [E_{\mathrm{exch}}^{(10)}]_{\mathrm{exch}} \\ &\quad + [E_{\mathrm{ind,resp}}^{(20)} + p_{\mathrm{ex}}(3.0)E_{\text{exch-ind,resp}}^{(20)} + \delta E_{\mathrm{HF}}^{(2)}]_{\mathrm{ind}} \\ &\quad + [E_{\mathrm{disp}}^{(20)} + p_{\mathrm{ex}}(3.0)E_{\text{exch-disp}}^{(20)}]_{\mathrm{disp}} \end{aligned} \tag{5}$$

Here, the value of $\delta E_{\mathrm{HF}}^{(2)}$ computed with $p_{\mathrm{ex}}(\alpha = 1)$ is left unchanged, and the $p_{\mathrm{ex}}(\alpha)$ scaling factor is also applied to $E_{\text{exch-disp}}^{(20)}$. Parker et al.[43] have called *s*SAPT0/jaDZ the "bronze standard" of SAPT,[43] where the jun-cc-pVDZ (jaDZ) basis set[58] has also been recommended for use with SAPT0.[28]

Schäffer and Jansen[45] have shown that $E_{\mathrm{exch}}^{(10)}$ and $E_{\text{exch-ind,resp}}^{(20)}$ are underestimated by the SEA, while $E_{\text{exch-disp}}^{(20)}$ is generally overestimated. Thus, the $p_{\mathrm{ex}}(\alpha)$ scaling factor based on first-order exchange is suitable for use with $E_{\text{exch-ind,resp}}^{(20)}$ but not $E_{\text{exch-disp}}^{(20)}$. As such, the fact that good results are obtained using *s*SAPT0, despite the fact that $E_{\text{exch-disp}}^{(20)}$ is scaled *up*, suggests that the success of this "bronze standard" rests on error cancellation. In this study, we will compare the effects of the SEA on the $E_{\mathrm{exch}}^{(10)}$, $E_{\text{exch-ind,resp}}^{(20)}$, and $E_{\text{exch-disp}}^{(20)}$ terms for ionic systems, and explore what is the best α value to use in scaling $E_{\text{exch-ind,resp}}^{(20)}$.

The SAPT2 method extends SAPT0 by including intramolecular electron correlation up to second order for electrostatic, exchange, and induction interactions (only). It is therefore only suitable for systems whose binding is dominated by electrostatics. The performance of SAPT2 is similar to that of MP2, and its energy expression is as follows:

$$\begin{aligned} E_{\mathrm{int}}^{\mathrm{SAPT2}} &= E_{\mathrm{int}}^{\mathrm{SAPT0}} + [E_{\mathrm{elst,resp}}^{(12)}]_{\mathrm{elst}} + [E_{\mathrm{exch}}^{(11)} + E_{\mathrm{exch}}^{(12)}]_{\mathrm{exch}} \\ &\quad + [{}^{t}E_{\mathrm{ind}}^{(22)} + {}^{t}E_{\text{exch-ind}}^{(22)}]_{\mathrm{ind}} \end{aligned} \tag{6}$$

The $E_{\mathrm{exch}}^{(11)}$ and $E_{\mathrm{exch}}^{(12)}$ terms are still based on the SEA. The superscript "*t*" in ${}^{t}E_{\mathrm{ind}}^{(22)}$ indicates that this is the "true" correlation part of $E_{\mathrm{ind}}^{(22)}$ not included in $E_{\mathrm{ind,resp}}^{(20)}$. The corresponding "true" correlation part of $E_{\text{exch-ind}}^{(22)}$ is estimated as

$${}^{t}E_{\text{exch-ind}}^{(22)} = {}^{t}E_{\mathrm{ind}}^{(22)}\left(\frac{E_{\text{exch-ind,resp}}^{(20)}}{E_{\mathrm{ind,resp}}^{(20)}}\right) \tag{7}$$

where $E_{\text{exch-ind,resp}}^{(20)}$ is based on the SEA; therefore, the ${}^{t}E_{\text{exch-ind}}^{(22)}$ is also based on the SEA. Although the δMP2 term (as shown below) often cancels the SEA employed in ${}^{t}E_{\text{exch-ind}}^{(22)}$, we will discuss the influence of the SEA for ${}^{t}E_{\text{exch-ind}}^{(22)}$ in normal SAPT calculations that do not employ the δMP2 correction term. Furthermore, the addition of the δMP2 term offers a means to correct the SEA in $E_{\text{exch-disp}}^{(20)}$, as shown below.

Three higher-level SAPT methods will also be studied: SAPT2+, SAPT2+(3), and SAPT2+3. These approaches include intramolecular electron correlation for dispersion up to second order; this is equivalent to MP4-level dispersion and scales as $O(N^7)$. The corresponding energy expressions are as follows:[17]

$$E_{\mathrm{int}}^{\mathrm{SAPT2+}} = E_{\mathrm{int}}^{\mathrm{SAPT2}} + [E_{\mathrm{disp}}^{(21)} + E_{\mathrm{disp}}^{(22)}]_{\mathrm{disp}} \tag{8}$$

$$E_{\mathrm{int}}^{\mathrm{SAPT2+(3)}} = E_{\mathrm{int}}^{\mathrm{SAPT2+}} + [E_{\mathrm{elst,resp}}^{(13)}]_{\mathrm{elst}} + [E_{\mathrm{disp}}^{(30)}]_{\mathrm{disp}} \tag{9}$$

$$\begin{aligned} E_{\mathrm{int}}^{\mathrm{SAPT2+3}} &= E_{\mathrm{int}}^{\mathrm{SAPT2+(3)}} + [E_{\mathrm{ind,resp}}^{(30)} + E_{\text{exch-ind,resp}}^{(30)}]_{\mathrm{ind}} \\ &\quad + [E_{\text{exch-disp}}^{(30)} + E_{\text{ind-disp}}^{(30)} + E_{\text{exch-ind-disp}}^{(30)}]_{\mathrm{disp}} \end{aligned} \tag{10}$$

aaThe SAPT2+3 method includes the coupling between induction and dispersion. The second-order correction $\delta E_{\mathrm{HF}}^{(2)}$ is replaced by the third-order $\delta E_{\mathrm{HF}}^{(3)}$ correction in SAPT2+3:

$$\begin{aligned} \delta E_{\mathrm{HF}}^{(3)} &= E_{\mathrm{int}}^{\mathrm{HF}} - (E_{\mathrm{elst}}^{(10)} + E_{\mathrm{exch}}^{(10)} + E_{\mathrm{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} \\ &\quad + E_{\mathrm{ind,resp}}^{(30)} + E_{\text{exch-ind,resp}}^{(30)}) \end{aligned} \tag{11}$$

The $E_{\text{exch-ind,resp}}^{(30)}$, $E_{\text{exch-disp}}^{(30)}$, and $E_{\text{exch-ind-disp}}^{(30)}$ terms are still based on the SEA, which is probably acceptable since $E_{\text{exch-disp}}^{(30)}$ is much smaller than $E_{\text{exch-disp}}^{(20)}$, and $E_{\text{exch-ind-disp}}^{(30)}$ is mostly canceled out by the corresponding $E_{\text{ind-disp}}^{(30)}$ term. Furthermore, the $\delta E_{\mathrm{HF}}^{(3)}$ terms often cancel the SEA used in $E_{\text{exch-ind,resp}}^{(30)}$. Parker et al.[43] have called SAPT2+/aug-cc-pVDZ the "silver standard" in SAPT.

The "δMP2" correction that was mentioned above is intended to account for missing terms such as high-order coupling between induction and dispersion.[43] This correction was defined as

$$\delta E_{\mathrm{MP2}} = E_{\mathrm{int}}^{\mathrm{MP2}} - E_{\mathrm{int}}^{\mathrm{SAPT2}} \tag{12}$$

where $E_{\mathrm{int}}^{\mathrm{MP2}}$ is the CP-corrected MP2 binding energy for the dimer, and $E_{\mathrm{int}}^{\mathrm{SAPT2}}$ contains the δHF correction, according to eqs 2 and 6. (Somewhat arbitrarily, the δMP2 term is grouped with the induction terms in the energy decomposition proposed in ref 43.) The δMP2 term can be incorporated into SAPT2+, SAPT2+(3), or SAPT2+3, affording methods that we will call SAPT2+δMP2, SAPT2+(3)-δMP2, and SAPT2+3-δMP2. This is equivalent to replacing $E_{\mathrm{int}}^{\mathrm{SAPT2}}$ in eqs 8– 10 with $E_{\mathrm{int}}^{\mathrm{MP2}}$. In other words, the three methods mentioned above, with the addition of δE_{MP2}, are effectively supermolecular MP2 plus a few additional SAPT terms. Parker et al.[43] have called SAPT2+(3)-δMP2/aug-cc-pVTZ the "gold standard" in SAPT. One can also compute dispersion with doubles amplitudes from a coupled-cluster doubles (CCD) calculation,[59,60] and for the three higher-order wave function-based SAPT methods, this addendum leads to methods called SAPT2+(CCD), SAPT2+(3)(CCD), and SAPT2+3(CCD).

Finally, we will consider DFT-SAPT calculations in which the interaction energy is

$$\begin{aligned} E_{\mathrm{int}}^{\text{DFT-SAPT}} &= [E_{\mathrm{elst}}^{(1)}]_{\mathrm{elst}} + [E_{\mathrm{exch}}^{(1)}]_{\mathrm{exch}} \\ &\quad + [E_{\mathrm{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + \delta E_{\mathrm{HF}}^{(2)}]_{\mathrm{ind}} \\ &\quad + [E_{\mathrm{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}]_{\mathrm{disp}} \end{aligned} \tag{13}$$

Here, the single superscript index indicates that intramolecular electron correlation is not included perturbatively but rather via DFT. Induction and dispersion energies in DFT-SAPT are determined at the coupled-perturbed static and frequency-dependent Kohn−Sham levels, respectively.

B. Data Sets and Benchmarks. We first computed binding energies for the pre-existing "IHB15" data set of 15 ionic hydrogen-bonded dimers,[61] in which the ion is acetate, guanidinium, methylammonium, or imidazolium. These calculations were performed at the SAPT2+(3)/aug-cc-pVTZ level to establish benchmarks for the individual energy components, as in previous benchmark studies.[50,62,63] The "gold standard" of SAPT methods,[43] namely, SAPT2+(3)-δMP2, was also used to establish the accuracy of these benchmarks. CCSD(T) energies extrapolated to the complete basis-set (CBS) limit are also available for the IHB15 data set.[61] The binding energies in this data set average −17.42 kcal/mol for the three anionic systems and −20.06 kcal/mol for the 12 cationic systems, computed at the CCSD(T)/CBS level. The mean absolute error (MAE) for SAPT2+(3)/aug-cc-pVTZ, relative to these CCSD(T)/CBS benchmarks, is 0.71 kcal/mol for the anions, 0.18 kcal/mol for the cations, and 0.28 kcal/mol overall.

Adding the δMP2 correction to SAPT2+(3)/aug-cc-pVTZ [to obtain the method that we call SAPT2+(3)-δMP2] reduces the MAE of the IHB15 data set to 0.16 kcal/mol (0.19 kcal/mol for the anions and 0.15 kcal/mol for the cations). The mean absolute contribution of the δMP2 correction is 0.90 kcal/mol for the anions and 0.20 kcal/mol for the cations. Notably, this correction is more significant for the anions and suggests that it would be useful to possess a data set with more than three different anions. For this reason, we have assembled a new database "AHB21" of CCSD(T)/CBS benchmark for 21 hydrogen-bonded dimers consisting of an anion and a neutral molecule. The anions in AHB21 are F^-, Cl^-, $N_3{}^-$, SH^-, and $HCOO^-$, and the dimers assembled from these anions are shown in Table 1 along with benchmark CCSD(T)/CBS binding energies, which range from −65.68 kcal/mol for $F^-(HF)$ to −7.97 kcal/mol for $N_3^-(NH_3)$. (Coordinates for all three of the data sets introduced here can be found in the Supporting Information.)

The three most strongly bound complexes in the AHB21 set are $F^-(HF)$, $Cl^-(HCl)$, and $OH^-(H_2O)$, with binding energies of −65.68, −41.79, and −37.31 kcal/mol, respectively. Consistent with solution-phase experiments for $(FHF)^-$,[64] each of these species is characterized by a proton that is shared equally between two heavy atoms (single minimum on the potential surface for proton transfer between the two X^- moieties). The strength of the $X^- \cdots H^+$ interaction and the symmetry of the complex drive the noncovalent interaction closer to a *covalent* interaction, resulting in a much larger binding energy as compared to the rest of the AHB21 data set. This characteristic also makes the definition of fragments ambiguous in these three systems, which may therefore be difficult test cases for SAPT and other fragment-based methods.

To complement the AHB21 set of anions, we have also assembled a cation-binding data set that we designate as "CHB6," which includes three alkali–water and three alkali–benzene complexes (see Table 1). Binding energies for CHB6 range from −39.09 kcal/mol for $Li^+(C_6H_6)$ to −17.83 kcal/mol for $K^+(H_2O)$.

Finally, we wish to consider cation/anion pairs. Zahn et al.[65] recently reported CCSD(T)/CBS binding energies for an "IL-2013" database consisting of 236 different pairs of cations and anions commonly encountered in ionic liquids (IL). The smallest 16 of these ion-pair structures are shown in Figure 1 and constitute what we will call the "IL16" data set. CCSD(T)/CBS binding energies for IL16 are listed in Table 2 and range from −87.42 to −120.80 kcal/mol. Note that the binding energies in

Table 1. CCSD(T)/CBS Binding Energy Benchmarks for the AHB21 and CHB6 Ion−Neutral Data Sets

no.	system	binding energy (kcal mol^{-1})
	AHB21	
1	$F^-(NH_3)$	−17.79
2	$F^-(H_2O)$	−32.50
3	$F^-(HF)$	−65.68
4	$Cl^-(NH_3)$	−8.98
5	$Cl^-(H_2O)$	−15.61
6	$Cl^-(HF)$	−25.52
7	$Cl^-(H_2S)$	−14.35
8	$Cl^-(HCl)$	−41.79
9	$OH^-(NH_3)$	−17.03
10	$OH^-(H_2O)$	−37.31
11	$N_3^-(NH_3)$	−7.97
12	$N_3^-(H_2O)$	−14.13
13	$N_3^-(HF)$	−26.01
14	$N_3^-(H_2S)$	−11.07
15	$SH^-(NH_3)$	−8.62
16	$SH^-(H_2O)$	−15.73
17	$SH^-(HF)$	−26.24
18	$HCO_2^-(CH_3NH_2)$	−12.80
19	$HCO_2^-(CH_3OH)$	−20.65
20	$HCO_2^-(H_2O)$	−21.03
21	$HCO_2^-(HF)$	−31.40
	CHB6	
22	$Li^+(H_2O)$	−34.43
23	$Na^+(H_2O)$	−23.83
24	$K^+(H_2O)$	−17.83
25	$Li^+(C_6H_6)$	−39.09
26	$Na^+(C_6H_6)$	−25.63
27	$K^+(C_6H_6)$	−19.90

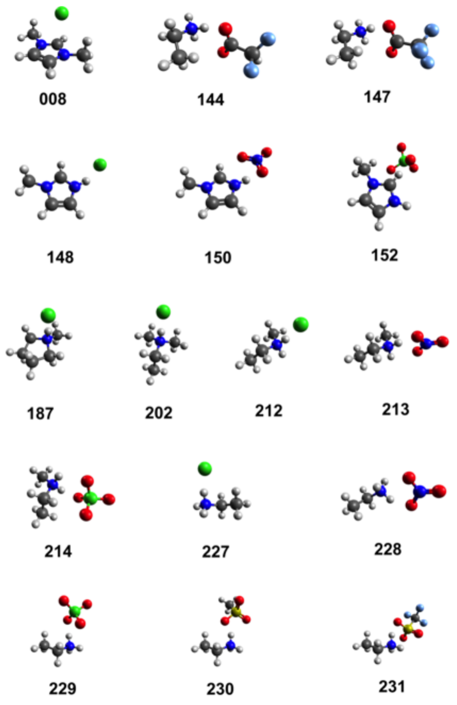


Figure 1. Structures of the cation/anion complexes in the IL16 data set, which were taken (along with the numbering scheme) from ref 65. The coloring system is as follows: white spheres (hydrogen), gray (carbon), dark blue (nitrogen), red (oxygen), pale blue (fluorine), green (chlorine), yellow (sulfur).

DOI: 10.1021/ct5010593
J. Chem. Theory Comput. 2015, 11, 2473−2486

Table 2. CCSD(T)/CBS Binding Energy Benchmarks for the IL16 Data Set

system[a]	binding energy (kcal mol^{-1})
IL-008	−100.41
IL-144	−120.80
IL-147	−116.91
IL-148	−105.01
IL-150	−104.44
IL-152	−87.42
IL-187	−114.00
IL-202	−113.51
IL-212	−114.91
IL-213	−112.75
IL-214	−104.47
IL-227	−118.19
IL-228	−112.02
IL-229	−106.53
IL-230	−110.98
IL-231	−102.37

[a] Nomenclature is taken from ref 65, and the structures are shown in Figure 1.

AHB21, CHB6, and IL16 data sets are considerably larger, on average, as compared to more established databases of neutral dimers, such as S22 or S66.[66,67]

C. Computational Methods. All geometries in the AHB21 and CHB6 data sets were optimized with the resolution-of-identity MP2 method using the aug-cc-pVTZ (aTZ) basis set, except that the def2-TZVPP basis set was used for the alkali atoms. [Similarly, in what follows def2-QZVPP is used for the alkali atoms in cases where aug-cc-pVQZ (aQZ) is used for the remaining atoms.] These geometry optimizations employed Q-CHEM v. 4.2.[68] The geometries of the IL16 data set were taken from ref 65. Subsequent single-point MP2 and CCSD(T) calculations were carried out using the Beta5 version of the PSI4 program,[69] and CCSD(T)-F12 calculations for $HCOO^-$ complexes were performed using the ORCA 3.0.2 program.[70] The CCSD(T)-F12 and MP2-F12 calculations for complexes in IL16 were computed using the MOLPRO 2012.1 program.[71]

Regarding the accuracy of CCSD(T)/CBS benchmarks in general for noncovalent interactions, note two recent studies by Hobza and co-workers that have gone beyond this level for small dimers.[4,5] In one of these studies, CCSD(T) binding energies were found to differ by no more than 0.1 kcal/mol (and typically much less) from coupled-cluster results containing connected quintuple excitations (CCSDTQP).[5] Another study considered contributions arising from core correlation, relativistic effects, and higher-order excitations at the level of CCSDT(Q), yet the sum total of these effects altered CCSD(T)/CBS binding energies by no more than 0.04 kcal/mol.[4]

For dimers in the AHB21 data sets that involve F^-, Cl^-, OH^-, N_3^-, and SH^-, as well as for the alkali−water complexes in CHB6, the CCSD(T) correlation energy in the CBS limit was estimated using a two-point (aTZ/aQZ) extrapolation scheme.[72] This correlation energy was then added to the Hartree−Fock/aQZ energy to obtain the CCSD(T)/CBS energy.

For the $HCOO^-$ complexes in the AHB21 data set, CCSD(T)-F12 correlation energies in the CBS limit were estimated using a two-point extrapolation (cc-pVDZ-F12/cc-pVTZ-F12 with the corresponding near-complete auxiliary basis sets cc-pVDZ-F12-CABS and cc-pVTZ-F12-CABS).[73,74] This correlation energy was added to the Hartree−Fock/cc-pVTZ-F12 energy including the HF-F12 basis set correction[75,76] to estimate the CCSD(T)/CBS energy.

For the three alkali−benzene complexes, the MP2 correlation energies in the CBS limit were estimated using a two-point (aTZ/aQZ) extrapolation, and this correlation energy was added to the Hartree−Fock/aQZ energy to estimate the MP2/CBS energy. In this case, we then add a triples correction:

$$\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}} = E_{\mathrm{CCSD(T)}} - E_{\mathrm{MP2}} \qquad (14)$$

The basis set used to evaluate this correction consists of def2-TZVPP for the alkali atoms and the “heavy augmented” (haTZ) basis set for the remaining atoms, in which the diffuse functions on hydrogen in aTZ are removed.

For the 16 complexes in the IL16 data set, the same MP2 extrapolation scheme as described above has been used to calculate the MP2/CBS energy. A triples correction, $\delta_{\mathrm{MP2\text{-}F12}}^{\mathrm{CCSD(T)\text{-}F12}}$, was estimated as the energy difference between CCSD(T)-F12 and MP2-F12 methods using the aDZ basis set. We expect that the quality of these CCSD(T)/CBS benchmarks is better than that of the original IL-2013 benchmarks,[65] in which the MP2 energy was extrapolated to CBS limit using basis sets lacking in diffuse functions (cc-pVTZ/cc-pVQZ), and moreover, the $\delta_{\mathrm{MP2}}^{\mathrm{CCSD(T)}}$ correction was estimated using a double-ζ basis set with no diffuse functions. The MAE between our new CCSD(T)/CBS benchmarks (Table 2) and the old ones (ref 65) is 0.19 kcal/mol, with a maximum deviation of 0.41 kcal/mol.

To determine the usefulness of wave function-based SAPT for ionic systems, we will compare the benchmark CCSD(T)/CBS binding energies to SAPT2+, SAPT2+(3), and SAPT2+3 results, both with and without CCD amplitudes for dispersion. These SAPT calculations were performed using Dunning’s aug-cc-pVXZ basis sets.[77,78] (As mentioned above, Ahlrichs’ def2-SVP, def2-TZVPP, and def2-QZVPP basis sets are used for the alkali atoms,[79] but we will continue to abbreviate these basis sets as aDZ, aTZ, and aQZ.) For alkali−benzene dimers, the aQZ calculations strain our computational resources, so in these cases the heavy-aug-cc-pVQZ (haQZ) basis set is used in place of the full aQZ basis, where diffuse functions on hydrogen are omitted. Note that the significantly diminished BSSE in SAPT calculations makes extrapolation to the CBS limit less important than it is for supersystem methods, and in fact, previous work has suggested that DFT-SAPT/aQZ calculations are essentially converged to the basis set limit.[80] Results presented here for the AHB21 data sets show only minor differences between SAPT/aTZ and SAPT/aQZ results, although the SAPT/aTZ outliers are slightly larger for the CHB6 data set. In any case, because the IL16 dimers are somewhat larger than those in the AHB21 and CHB6 data sets, we omit the high-level SAPT/aQZ calculations for this particular data set.

The SAPT0/jaDZ and *s*SAPT0/jaDZ methods will also be evaluated for our three data sets. (The jaDZ basis set was recommended for SAPT0 calculations by Sherrill and co-workers.[28,43] The same basis has also been called aug-cc-pVDZ′ and removes a subset of the diffuse functions from aDZ.) Truncations of the virtual space based on MP2 natural orbitals were used to reduce the cost of the SAPT2+, SAPT2+(3), and SAPT2+3, as described in refs 27 and 60. Density fitting, as implemented in PSI4, was used in all SAPT calculations. The SAPT2 and CP-corrected MP2 binding energies required for the δMP2 correction were also performed with the PSI4 program.[69] The exact second-order (non-SEA) terms $E_{\mathrm{exch\text{-}ind,resp}}^{(20)}$ and $E_{\mathrm{exch\text{-}disp}}^{(20)}$ were evaluated using a locally modified version of the MOLPRO 2012.1 program.[71]

Table 3. Mean Absolute Errors[a] (MAEs) and Maximum Errors in the Single-Exchange (S^2) Approximation[b]

	error (kcal mol^{-1})								
	AHB21			CHB6			IL16		
		maximum			maximum			maximum	
exchange term	MAE	value	system	MAE	value	system	MAE	value	system
				HF-SAPT					
$E^{(10)}_{\text{exch}}(S^2)$	1.05	6.35	$Cl^-(HCl)$	0.03	0.05	$Li^+(H_2O)$	0.98	1.71	IL-202
$E^{(20)}_{\text{exch-ind,resp}}(S^2)$	1.05	8.44	$Cl^-(HCl)$	0.06	0.10	$Li^+(C_6H_6)$	1.28	2.59	IL-008
$p_{\text{ex}}(\alpha = 2.04)\ E^{(20)}_{\text{exch-ind,resp}}(S^2)$	0.07	0.31	$F^-(HF)$	0.00	0.01	$K^+(C_6H_6)$	0.08	0.15	IL-213
$E^{(20)}_{\text{exch-disp}}(S^2)$	0.07	0.35	$F^-(HF)$	0.00	0.01	$K^+(C_6H_6)$	0.03	0.06	IL-202
${}^{t}E^{(22)}_{\text{exch-ind}}(S^2)$	0.11	0.49	$F^-(HF)$	0.00	0.01	$K^+(H_2O)$	0.15	0.25	IL-202
$p_{\text{ex}}(\alpha = 2)\ {}^{t}E^{(22)}_{\text{exch-ind}}(S^2)$	0.01	0.07	$F^-(HF)$	0.00	0.00	$Li^+(H_2O)$	0.02	0.04	IL-213
				DFT-SAPT					
$E^{(1)}_{\text{exch}}(S^2)$	1.15	6.31	$Cl^-(HCl)$	0.03	0.06	$Li^+(H_2O)$	1.11	1.77	IL-202
$E^{(2)}_{\text{exch-ind}}(S^2)$	1.33	9.28	$Cl^-(HCl)$	0.07	0.10	$Li^+(H_2O)$	1.69	3.36	IL-008
$p_{\text{ex}}(\alpha = 2.07)\ E^{(2)}_{\text{exch-ind}}(S^2)$	0.09	0.83	$Cl^-(HCl)$	0.00	0.01	$K^+(C_6H_6)$	0.10	0.16	IL-202
$E^{(2)}_{\text{exch-disp}}(S^2)$	0.11	0.52	$F^-(HF)$	0.00	0.01	$K^+(C_6H_6)$	0.07	0.11	IL-202

[a] Error is defined with respect to the exact first- or second-order exchange energy. [b] The aTZ basis set is used here, but aDZ and aQZ results can be found in the Supporting Information.

DFT-SAPT calculations employ Kohn−Sham (KS) orbitals determined using the PBE0AC exchange-correlation (XC) potential.[32] A hybrid XC kernel consisting of 25% exact exchange and 75% of the adiabatic local density approximation[81] was used to solve coupled-perturbed static and frequency-dependent KS equations for the second-order contributions. The shift parameter in the asymptotic correction[82] was computed in each case using PBE0/aQZ calculations for the neutral molecules and PBE0/def2-QZVPP for the cations. The anionic systems were left without asymptotic correction since the XC potentials in these cases are short-ranged and do not decay as $1/r$.[83] The $\delta E^{(2)}_{\text{HF}}$ correction is included in DFT-SAPT to estimate polarization effects beyond second order. All DFT-SAPT calculations were performed using a locally modified version of the MOLPRO 2012.1 program.[71] Again due to the larger size of the IL16 dimers, the HF-SAPT and DFT-SAPT calculations with exact second-order exchange were limited to the aTZ basis set in these cases.

We will also take the opportunity to test some density-functional methods for AHB21, CHB6, and IL16. Among density functionals, M06-2X,[6] ωB97X-D,[84] ωB97X-D3,[85] LC-VV10,[11] ωB97X-V,[86] and B97M-V[87] will be tested because they have shown good performance for noncovalent interactions in neutral systems.[51,85−87] Their performance for ionic systems is suspect, however, in view of previous calculations on $SO_4^{2-}(H_2O)_n$, $F^-(H_2O)_n$, and $Cl^-(H_2O)_n$ clusters,[50,86,88] where the root-mean-square deviations for binding energies were in some cases as large as 4.8 kcal/mol (M06-2X), 1.3 kcal/mol (ωB97X-D), and 2.7 kcal/mol (LC-VV10), although both ωB97X-V and B97M-V exhibit errors no larger than 0.5 kcal/mol.[87]

To the best of our knowledge, the ωB97X-D3 method has not been used to calculate the binding energies in ionic systems but will be tested here. The aTZ basis set (with def2-TZVPP for alkali atoms, as usual) was used in all DFT calculations, along with a ($N_r = 99$; $N_\Omega = 590$) Euler−Maclaurin−Lebedev quadrature grid for the semilocal functionals and a (75,302) grid for the nonlocal contributions to LC-VV10, ωB97X-V, and B97M-V.

Finally, we test a recently developed Coulomb-attenuated MP2 method (att-MP2).[46−49] This approach splits the two-electron Coulomb operator into short- and long-range components,[89] then neglects the long-range part in an effort to eliminate BSSE. We use the aTZ basis set for all att-MP2 calculations (def2-TZVPP for the alkali atoms) since the attenuation parameter was fitted using aTZ and since att-MP2/aTZ calculations yield accurate intermolecular interaction energies in neutral dimers, and att-MP2/aQZ results offer only a very tiny improvement that does not justify the increased cost.[47]

MP2/aTZ, MP2/aQZ, and MP2/CBS binding energies are also reported, using a two-point extrapolation scheme. All supersystem calculations are counterpoise corrected except for the DFT and att-MP2 calculations. (DFT/aTZ results are likely close to the basis-set limit already, and att-MP2 is designed to eliminate BSSE, so it does not make sense to apply a counterpoise correction in this case.)

III. RESULTS AND DISCUSSION

A. Accuracy of the S^2 Approximation. Given the importance of exchange effects beyond the SEA for anions,[38] we first examine the accuracy of the exchange, exchange−induction, and exchange−dispersion interactions within the S^2 approximation. Table 3 presents the errors in these energy components for our three data sets, where "error" is defined with respect to the corresponding exact (non-SEA) energy components. (These results are obtained using the aTZ basis, but similar behavior is observed using aDZ and aQZ, and these data can be found in the Supporting Information.) In keeping with the observations of Schäffer and Jansen for neutral systems and a few ions,[44,45] we find that the SEA underestimates the first-order exchange energy and the second-order exchange-induction energy, whereas $E^{(20)}_{\text{exch-disp}}(S^2)$ is too large.

For the cationic dimers, the S^2 approximation engenders very little error in $E^{(10)}_{\text{exch}}(S^2)$, $E^{(20)}_{\text{exch-ind}}(S^2)$, or $E^{(20)}_{\text{exch-disp}}(S^2)$. For the anions, however, the $E^{(10)}_{\text{exch}}(S^2)$ and $E^{(20)}_{\text{exch-ind}}(S^2)$ terms exhibit large errors, with MAEs of 1 kcal/mol and maximum errors as large as 6−9 kcal/mol in the case of $Cl^-(HCl)$. However, $E^{(20)}_{\text{exch-disp}}(S^2)$ is quite accurate for anions, with maximum errors $\lesssim$0.5 kcal/mol. For the ion pairs, the MAE for the $E^{(10)}_{\text{exch}}(S^2)$ term is similar to that obtained for the AHB21 data set. However, the MAE for $E^{(20)}_{\text{exch-ind}}(S^2)$ in IL16 is about 0.4 kcal/mol larger than that in AHB21. Maximum errors in $E^{(10)}_{\text{exch}}(S^2)$ and $E^{(20)}_{\text{exch-ind}}(S^2)$ are generally smaller for IL16 as compared to AHB21, as the ion-pair data set does not contain any of the symmetric shared-proton complexes, $X^{-}\cdots H^{+}\cdots X^{-}$, that are so difficult for SAPT-based methods. The $E^{(20)}_{\text{exch-disp}}(S^2)$ term is very accurate for IL16, with a maximum error of only 0.06 kcal/mol.

For the wave function-based HF-SAPT method, we will scale $E^{(20)}_{\text{exch-ind,resp}}(S^2)$ by $p_{\text{ex}}(\alpha)$, where an optimal value $\alpha = 2.04$ was determined by minimizing the MAE (with respect to exact values of $E^{(20)}_{\text{exch-ind,resp}}$) for the AHB21 data set. This optimal value is consistent with the value $\alpha = 2$ that we used for $F^{-}(H_2O)$ in a previous study,[38] and for the full AHB21 data set, scaling with $\alpha = 2.04$ affords a MAE of only 0.07 kcal/mol for the $E^{(20)}_{\text{exch-ind,resp}}(S^2)$ term, with a maximum error of 0.3 kcal/mol for $F^{-}(HF)$. The optimal scaling value for DFT-SAPT calculations is similar ($\alpha = 2.07$), and errors in the scaled DFT-SAPT value of $E^{(2)}_{\text{exch-ind}}(S^2)$ are also small. For the IL16 data set, an optimal value $\alpha = 2.20$ was obtained for both HF-SAPT and DFT-SAPT calculations; the MAE for the scaled value of $E^{(20)}_{\text{exch-ind,resp}}(S^2)$ with $\alpha = 2.20$ is only 0.1 kcal/mol.

Typically, the ${}^{t}E^{(22)}_{\text{exch-ind}}$ term in eq 7 employs the SEA since $E^{(20)}_{\text{exch-ind,resp}}$ in eq 7 is based on the SEA as well. For the AHB21 and IL16 data sets, the MAEs in ${}^{t}E^{(22)}_{\text{exch-ind}}(S^2)$ based on the SEA are 0.11 and 0.15 kcal/mol, respectively, as compared to exact results. Scaling with $\alpha = 2$ reduces both the mean and maximum errors nearly to zero; see Table 3. Errors for the cation data set are even smaller.

To summarize, the S^2 approximation appears to be suitable for use in cation−neutral systems and also for the $E^{(20)}_{\text{exch-disp}}$ term in anion−neutral and ion-pair systems but not for $E^{(10)}_{\text{exch}}$ or $E^{(20)}_{\text{exch-ind,resp}}$ in anion−neutral and ion pair binding. Since exact second-order exchange formulas[44,45] have not yet been widely implemented in quantum chemistry codes, we recommend scaling the SEA versions of these terms by $p_{\text{ex}}(\alpha)$ in eq 4, with $\alpha = 2$. This approach will be taken in the subsequent SEA-based SAPT calculations in this work.

For calculations based on HF-SAPT, we also use a scaling factor of $p_{\text{ex}}(\alpha = 2)$ for $E^{(20)}_{\text{exch-ind,resp}}(S^2)$, and then this scaled value is used to obtain ${}^{t}E^{(22)}_{\text{exch-ind}}$ according to eq 7. For the DFT-SAPT methods, the closed-form analytic formula is used for $E^{(2)}_{\text{exch-disp}}$ and $E^{(2)}_{\text{exch-ind}}$ since the SEA and scaled SEA values exhibit somewhat larger maximum errors. Furthermore, the exact (non-SEA) $\delta E^{(2)}_{\text{HF}}$ correction will be used to obtain total binding energies with DFT-SAPT. For the *s*SAPT0 method, $p_{\text{ex}}(3.0)$ is used for both $E^{(20)}_{\text{exch-ind,resp}}$ and $E^{(20)}_{\text{exch-disp}}$ in eq 5, as proposed in ref 43. The δHF term can correct the SEA used in exchange−induction, and the δMP2 term can further correct the SEA used in $E^{(20)}_{\text{exch-disp}}(S^2)$ and ${}^{t}E^{(22)}_{\text{exch-ind}}(S^2)$.

B. AHB21 Anion−Neutral Data Set. Existing benchmarks for neutral systems suggest that SAPT0, the simplest SAPT method, performs well in conjunction with the jaDZ basis set in non-hydrogen-bonded systems, owing to favorable error cancellation.[28,43] For hydrogen-bonded systems, SAPT0/jaDZ exhibits a MAE of 1.26 kcal/mol and a maximum error of 6.68 kcal/mol, across four different data sets examined by Parker et al.[43] Almost all of these systems are overbound at the SAPT0/jaDZ level; hence, the errors are reduced by empirical scaling, i.e., the *s*SAPT0/jaDZ method of eq 5. This is the "bronze standard" of SAPT, and it affords a MAE of 0.71 kcal/mol and a maximum error of 1.55 kcal/mol for the same, neutral data set.[43]

The AHB21 systems exhibit even stronger hydrogen bonds, and for this data set, the MAE for SAPT0/jaDZ is 2.01 kcal/mol, and the maximum error is 9.54 kcal/mol. The most difficult systems are $F^{-}(HF)$, $Cl^{-}(HCl)$, and $OH^{-}(H_2O)$, for which the binding energies are overestimated by 9.54, 6.24, and 6.51 kcal/mol, respectively. Scaling of the exchange interactions only helps a little: the *s*SAPT0/jaDZ method affords a MAE of 1.58 kcal/mol and a maximum error of 7.58 kcal/mol for AHB21. These results suggest that low-order SAPT methods are not suitable for use in anionic systems with large binding energies.

Figures 2a and 2b show AHB21 error statistics for six high-level SAPT methods: SAPT2+, SAPT2+(3), and SAPT2+3, each with and without CCD amplitudes for dispersion. (Binding energies for each individual system at each level of theory are available in the Supporting Information.) Consistent with the trends observed by Parker et al.[43] for neutral hydrogen-bonded systems, we find that both the mean and maximum errors *increase* as the basis set is enlarged. [The only exception to this trend is a very slight decrease in the MAE going from aDZ to aTZ at the SAPT2+(3)(CCD) level.] The best-performing methods are SAPT2+/aDZ (MAE = 0.77 kcal/mol) and SAPT2+(CCD)/aDZ (MAE = 0.74 kcal/mol), and the maximum error for these two methods is 2.8 kcal/mol, for the $Cl^{-}(HCl)$ system. If the aTZ or aQZ basis set is employed, then SAPT2+(3)(CCD) affords the best performance. Use of CCD dispersion reduces the MAE when the aTZ or aQZ basis is used, although it actually causes a slight increase in the MAE when the basis set is aDZ. In the AHB21 data set, the silver standard SAPT method, SAPT2+/aDZ, performs better than the bronze standard, *s*SAPT0/jaDZ.

Replacing $E^{(20)}_{\text{exch-ind,resp}}$ with a scaled version thereof amounts to adding a term $[p_{\text{ex}}(\alpha)-1]\ E^{(20)}_{\text{exch-ind,resp}}$ to SAPT. The value of this scaled-exchange correction, along with that of $[p_{\text{ex}}(\alpha)-1]\ {}^{t}E^{(22)}_{\text{exch-ind}}$, is plotted in Figure 3a for each dimer in AHB21 and for $\alpha = 2$. These corrections are all similar in the aDZ, aTZ, and aQZ basis sets, so only aTZ results are shown in Figure 3. (The analogous plots for the aDZ and aQ basis sets can be found in the Supporting Information.) The values $\alpha = 1$ and $\alpha = 3$ also afford similar results, although the best-performing value of α is somewhat sensitive to the choice of basis set. MAEs for AHB21 computed at the SAPT2+3-δMP2 in various basis sets using either $\alpha = 1$ or $\alpha = 3$ can be found in the Supporting Information.

The exchange correction for $E^{(20)}_{\text{exch-ind,resp}}$ is significant especially for $F^{-}(HF)$, $Cl^{-}(HCl)$, and $OH^{-}(H_2O)$, where it contributes 2.3, 8.5, and 2.3 kcal/mol, respectively. These three systems are better described as $X^{-}\cdots H^{+}\cdots X^{-}$, in which a proton is shared equally between two anions, leading to $H^{+}\cdots X^{-}$ distances that are in the range of typical covalent bond lengths: 1.144 Å for X = F, 1.558 Å for X = Cl, and 1.359 Å for X = OH. The SAPT formalism, however, requires us to describe the system as $X^{-}\cdots HX$, and the short intermonomer distance leads to a severe breakdown of the SEA (see Table 3). As such, $E^{(10)}_{\text{exch}}$ is very different from $E^{(10)}_{\text{exch}}(S^2)$ for these three systems, and the scaled-exchange correction is large. However, the breakdown of the S^2 approximation or the large exchange correction for $E^{(20)}_{\text{exch-ind,resp}}$ can be mitigated by incorporating $\delta\ E^{(2)}_{\text{HF}}$, as has been pointed out before.[38] The exchange correction for ${}^{t}E^{(22)}_{\text{exch-ind}}$ is not large, with a maximum value among the AHB21 dimers of only 0.41 kcal/mol, for $Cl^{-}(HCl)$.

The large errors documented for AHB21 in Figure 2a can be remedied by adding the δMP2 correction (eq 12). The magnitude of this correction for each AHB21 dimer is shown in Figure 3a, from which we see that the δMP2 correction is also largest for the three $X^{-}\cdots H^{+}\cdots X^{-}$ systems, namely, 3.27, 5.79, and 3.43 kcal/mol for X = F, Cl, and OH, respectively. The large magnitude of this correction is another indication of breakdown of the perturbation series such that SAPT may not yield accurate energy components in such cases, as discussed also by Parker et al.[43] Total binding energies can still be reproduced accurately if

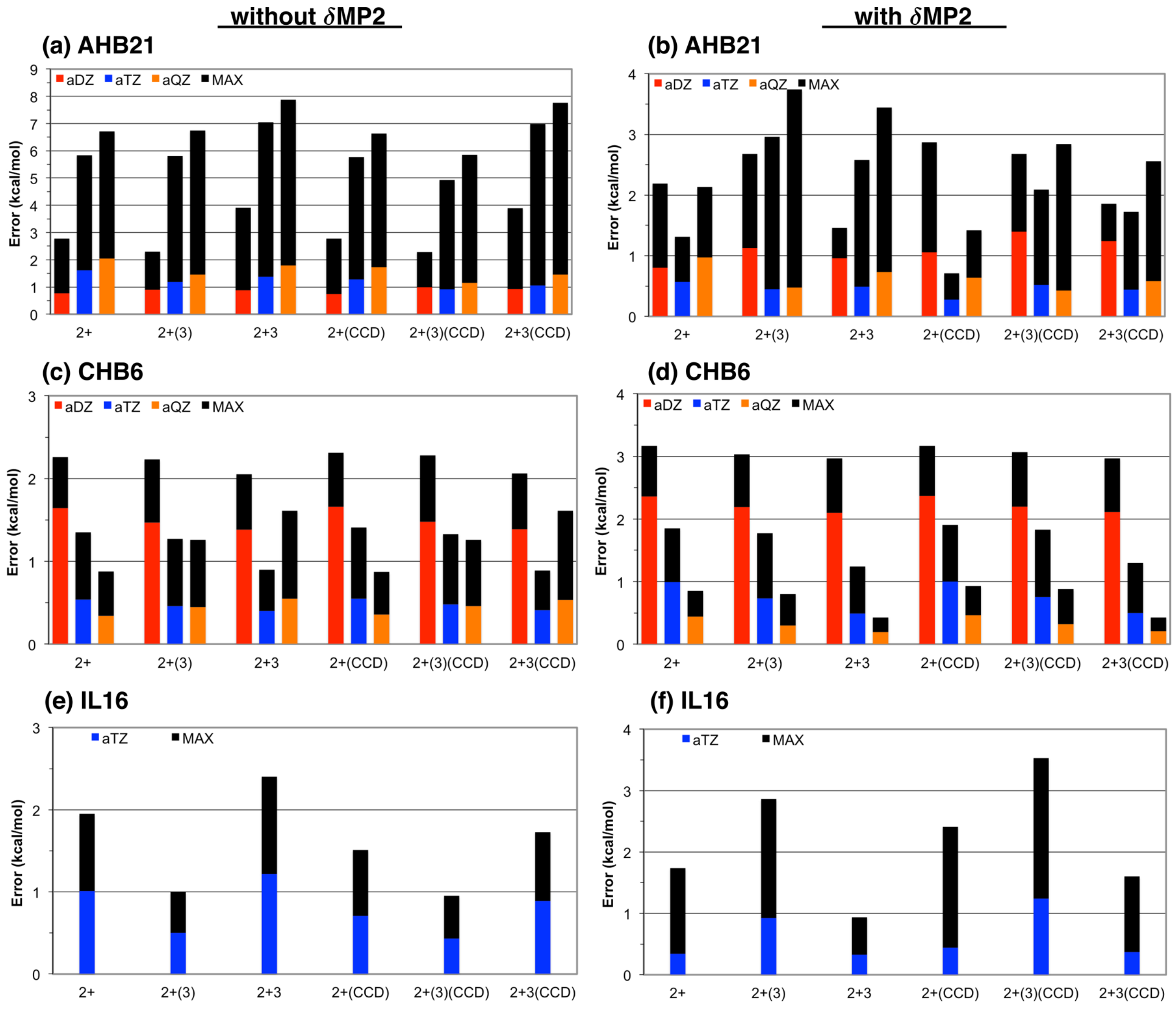


Figure 2. Mean absolute errors (MAEs, in red, blue, and orange) and maximum errors (in black) for different levels of SAPT as applied to the AHB21, CHB6, and IL16 databases of hydrogen-bonded ion−neutral and cation−anion dimers. For all terms based on the SEA, ${}^{t}E^{(22)}_{\text{exch-ind}}$ is scaled by $p_{\text{ex}}(\alpha = 2)$, $E^{(20)}_{\text{exch-ind}}$ is corrected by δHF, and $E^{(20)}_{\text{exch-disp}}$ is still based on the SEA. Panels on the right show the results when the δMP2 correction (eq 12) is included, whereas this correction is omitted in the panels on the left. Note that different panels use different vertical scales.

the δMP2 correction is included, as shown in Figure 2b and discussed below. Note that SAPT with the δMP2 correction is really just supermolecular MP2 with a few additional SAPT terms and that this correction can cancel out the SEA used in $E^{(20)}_{\text{exch-disp}}$ and ${}^{t}E^{(22)}_{\text{exch-ind}}$.

Comparing Figure 2b to 2a, we see that the δMP2 correction significantly reduces the errors at all levels of SAPT. The SAPT-δMP2 methods with the aTZ and aQZ basis sets outperform the corresponding methods with the aDZ basis, with SAPT-δMP2/aTZ being slightly more accurate than the corresponding aQZ method, except in the case of SAPT2+(3)-δMP2 and SAPT2+(3)(CCD)-δMP2. Among all of the SAPT methods evaluated here, the SAPT2+(CCD)-δMP2/aTZ approach provides the most accurate results for the AHB21 data set, with a MAE of 0.28 kcal/mol and a maximum error of 0.71 kcal/mol, which occurs in the case of $F^-(H_2O)$. The superior performance of SAPT2+(CCD)-δMP2/aTZ is in line with previous conclusions,[43] although the errors for these anion−neutral dimers are slightly larger than errors reported for neutral systems in ref 43. Note that SAPT2+(CCD)-δMP2 has also been called MP2(CCD) since it amounts to a supermolecular MP2 calculation supplemented with dispersion corrections from CCD amplitudes.[43]

In the four hydrogen-bonded systems examined by Parker et al.,[43] the MAE in SAPT2+(3)-δMP2/aTZ was 0.24 kcal/mol and was slightly worse than results at the SAPT2+(CCD)-δMP2/aTZ level (0.22 kcal/mol) and SAPT2+3-δMP2/aTZ level (0.21 kcal/mol). Nevertheless, those authors designate SAPT2+(3)-δMP2/aTZ as the "gold standard" of SAPT since the performance is similar, but the computational cost is ∼50% less than that of SAPT2+(CCD)-δMP2/aTZ. However, for the AHB21 data set, the SAPT2+(3)-δMP2/aTZ exhibits a MAE of 0.45 kcal/mol and a maximum error of 2.96 kcal/mol. This MAE is about twice as large as that obtained at the SAPT2+(CCD)-δMP2/aTZ level, and as such, we recommend SAPT2+(CCD)-δMP2/aTZ as the method of choice when a balanced description of both neutral and anionic hydrogen-bonded systems is required. The SAPT2+3-δMP2/aTZ method performs similar to SAPT2+(3)-δMP2/aTZ, with a MAE of 0.49 kcal/mol and maximum error of 2.6 kcal/mol.

Statistical errors in AHB21 binding energies obtained from DFT-SAPT calculations *without* the SEA are summarized in Table 4. The MAEs of DFT-SAPT decrease as the basis set is enlarged, becoming as small as 0.91 kcal/mol in the aQZ basis. The wave function-based SAPT2+(CCD)-δMP2/aTZ,

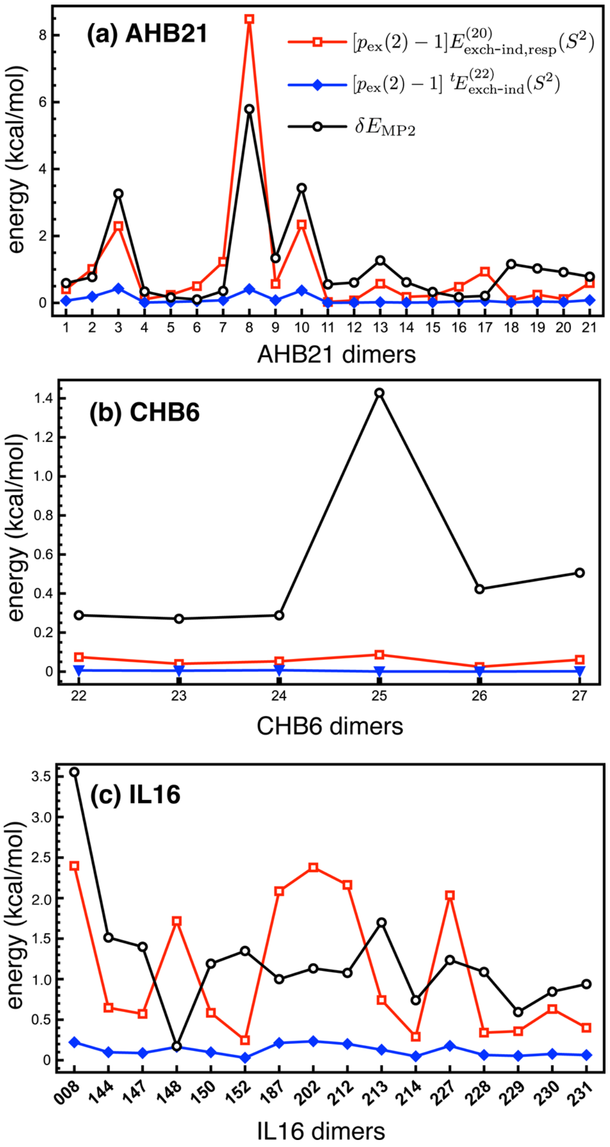


Figure 3. Magnitude of the δMP2 correction (eq 12), as well as the two second-order scaled-exchange corrections, using the aTZ data set. (Note that the various panels use different vertical scales.) The quantity $p_{\text{ex}}(\alpha)$ is the scaling factor defined in eq 4. The numbering system for the various dimers corresponds to that given in Table 1 (for AHB21 and CHB6) and Figure 1 (for IL16).

SAPT2+(3)-δMP2/aTZ, and SAPT2+3-δMP2/aTZ methods thus exhibit smaller MAEs and smaller maximum errors for AHB21, as compared to DFT-SAPT, although the latter approach is less expensive and can be made to scale as $O(N^5)$ with density fitting.[30,90]

For comparison, error statistics for AHB21 using MP2 and DFT methods are also listed in Table 4. The M06-2X and LC-VV10 methods, which have previously been recommended for DFT calculations of noncovalent interactions, afford MAEs in excess of 1 kcal/mol, as in previous studies of $F^-(H_2O)_n$ and $Cl^-(H_2O)_n$ clusters.[50,51] The ωB97X-D, ωB97X-D3, ωB97X-V, and B97M-V methods afford much smaller MAEs (0.3 kcal/mol), performance that is comparable to SAPT2+(CCD)-δMP2/aTZ. This result is consistent with the good performance of ωB97X-D/aTZ for other hydrogen-bonded systems.[91] As with most of the SAPT methods, the $X^-\cdots H^+\cdots X^-$ systems remain challenging and constitute the largest source of error for each density functional, as well as for each MP2 method.

Table 4. Mean Absolute Errors[a] (MAEs) and Maximum Errors in Binding Energies for the AHB21 Data Set

	error (kcal mol^{-1})		
		maximum	
method	MAE	value	system
SAPT2+(CCD)-δMP2/aTZ[b]	0.28	0.71	$F^-(H_2O)$
DFT-SAPT[c]/aDZ	1.93	5.73	$F^-(HF)$
DFT-SAPT[c]/aTZ	1.03	6.15	$Cl^-(HCl)$
DFT-SAPT[c]/aQZ	0.91	6.97	$Cl^-(HCl)$
DFT-SAPT[c]/CBS[d]	0.89	7.56	$Cl^-(HCl)$
M06-2X/aTZ	1.08	3.97	$F^-(HF)$
LC-VV10/aTZ	1.18	3.55	$Cl^-(HCl)$
ωB97X-D/aTZ	0.27	0.64	$OH^-(H_2O)$
ωB97X-D3/aTZ	0.32	0.98	$OH^-(H_2O)$
ωB97X-V/aTZ	0.32	0.99	$OH^-(H_2O)$
B97M-V/aTZ	0.29	1.29	$Cl^-(HCl)$
att-MP2/aTZ	0.47	2.47	$Cl^-(HCl)$
MP2/aTZ	0.67	1.96	$F^-(HF)$
MP2/aQZ	0.45	1.88	$Cl^-(HCl)$
MP2/CBS	0.40	2.64	$Cl^-(HCl)$

[a] With respect to CCSD(T)/CBS benchmarks. [b] Best-performing SAPT method for this data set. [c] Includes exact second-order exchange. [d] From aTZ/aQZ extrapolation of the dispersion contributions.

Regarding "attenuated" MP2 (att-MP2) methods,[46,89] we find that the att-MP2/aTZ results are superior to MP2/aTZ, consistent with results of a previous study.[47] However, MP2/aQZ and MP2/CBS results are slightly better still. The reason may be that the Coulomb attenuation parameter in att-MP2 that was reported in ref 47 (and used here) was optimized against the S66 data set,[67] which contains only charge-neutral monomers, and therefore, this attenuation parameter may not strike an ideal balance between neutral and ionic systems.

C. CHB6 Cation−Neutral Data Set. Errors in high-level SAPT methods applied to CHB6 are shown in Figures 2c and 2d, are much smaller than those obtained for AHB21 [Figure 2a]. This is consistent with results for Hobza's IHB15 data set,[61] for which the SAPT2+(3) /aTZ method exhibits large errors for the anionic dimers but performs much better for the cations. Unlike AHB21 results, for CHB6 the aTZ and aQZ basis sets afford much smaller errors as compared to results obtained using aDZ.

The scaled-exchange and δMP2 corrections for CHB6 are plotted in Figure 3b. (As for AHB21, the aDZ and aQZ results are given in the Supporting Information.) The two exchange corrections are close to zero, and the δMP2 correction is also not large, with a maximum value of 1.43 kcal/mol for $Li^+(C_6H_6)$. In this outlier, the distance from Li^+ to the center of the benzene ring is only 1.91 Å.

In contrast to the AHB21 dimers, for these cation−neutral systems the addition of δMP2 tends to increase the errors, except for SAPT2+(3)/aQZ and SAPT2+3/aQZ (with or without CCD dispersion); see Figure 2d. However, the δMP2 correction does cause SAPT to exhibit monotonic convergence toward the CBS limit, so that errors with respect to CCSD(T)/CBS results are the smallest in the largest basis sets. Notably, this monotonic convergence is *not* observed in the AHB21 data set; see Figure 2b. The cation−neutral complexes in CHB6 are also better behaved with respect to increasing the level of SAPT, i.e.,

$$\text{SAPT2+} \rightarrow \text{SAPT2+(3)} \rightarrow \text{SAPT2+3}$$

However, the more robust treatment of dispersion based on CCD amplitudes has little effect.

The best SAPT methods for the CHB6 data set are SAPT2+3/aQZ and SAPT2+3(CCD)/aQZ, which exhibit MAEs of 0.19 and 0.21 kcal/mol, respectively, and errors no larger than 0.43 kcal/mol [for $Li^+(H_2O)$]. The so-called gold and silver SAPT standards, SAPT2+(3)-δMP2/aTZ and SAPT2+/aDZ (respectively), afford MAEs of 0.73 and 1.64 kcal/mol, respectively. The SAPT2+(CCD)-δMP2/aTZ method, which we identified as the best approach for the AHB21 data set, exhibits a 1 kcal/mol MAE for CHB6, with a maximum error of 1.91 kcal/mol. SAPT2+3-δMP2/aTZ, identified by Parker et al.[43] as the best SAPT method for neutral hydrogen-bonded systems, still affords moderate errors for the CHB6 data set with a MAE of 0.49 kcal/mol and a maximum error of 1.24 kcal/mol. Hence, the extra coupling terms between induction and dispersion in SAPT2+3 as compared to SAPT2+(3) improve the binding description in cation−neutral complexes. For such systems, we therefore recommend the highest possible level of SAPT combined with the largest affordable basis set, preferably SAPT2+3/aQZ.

DFT-SAPT (with exact second-order exchange) shows monotonic convergence with respect to expansion of the basis set (see Table 5), as observed also for the AHB21 data set. However, the MAE at the DFT-SAPT/aQZ level is 0.56 kcal/mol, three times worse than the best wave function-based SAPT method, SAPT2+3-δMP2/aQZ, and slightly worse than SAPT2+3-δMP2/aTZ also. However, DFT-SAPT/aQZ does outperform the so-called silver- and gold standards of wave function-based SAPT.

Table 5. Mean Absolute Errors[a] (MAEs) and Maximum Errors in Binding Energies for the CHB6 Data Set[b]

	error ($kcal\ mol^{-1}$)		
		maximum	
method	MAE	value	system
SAPT2+3-δMP2/aQZ[c]	0.19	0.43	$Li^+(H_2O)$
DFT-SAPT[d]/aDZ	1.70	2.40	$Na^+(C_6H_6)$
DFT-SAPT[d]/aTZ	0.80	1.73	$K^+(C_6H_6)$
DFT-SAPT[d]/aQZ	0.56	1.10	$K^+(C_6H_6)$
DFT-SAPT[d]/CBS[e]	0.47	1.05	$Na^+(C_6H_6)$
M06-2X/aTZ	1.30	3.27	$Li^+(C_6H_6)$
LC-VV10/aTZ	1.62	4.60	$Li^+(C_6H_6)$
ωB97X-D/aTZ	0.76	0.97	$Li^+(H_2O)$
ωB97X-D3/aTZ	0.32	0.77	$K^+(H_2O)$
ωB97X-V/aTZ	0.71	2.25	$Li^+(C_6H_6)$
B97M-V/aTZ	0.85	1.55	$K^+(C_6H_6)$
att-MP2/aTZ	0.88	2.05	$Na^+(C_6H_6)$
MP2/aTZ	0.90	1.20	$K^+(C_6H_6)$
MP2/aQZ	0.31	0.55	$Na^+(C_6H_6)$
MP2/CBS	0.22	0.64	$K^+(C_6H_6)$

[a] With respect to CCSD(T)/CBS benchmarks. [b] For the alkali atoms, the def2-SVP (aDZ), def2-TZVPP (aTZ), and def2-QZVPP (aQZ) basis sets are used. [c] Best-performing SAPT method for this data set. [d] Includes exact second-order exchange. [e] From aTZ/aQZ extrapolation of the dispersion contributions.

Table 5 also reports error statistics for DFT and MP2-based methods as applied to the CHB6 data set. The M06-2X and LC-VV10 methods afford large MAEs (1.30 and 1.62 kcal/mol, respectively), much worse than the performance of these functionals for benchmark noncovalent interactions involving neutral molecules.[51] The ωB97X-D, ωB97X-V, and B97M-V methods give similar errors, with MAEs of 0.7−0.9 kcal/mol. Among the functionals tested here, ωB97X-D3 affords the smallest MAE (0.32 kcal/mol) for the CHB6 data set. However, the MP2/aQZ and MP2/CBS methods afford even smaller MAEs, 0.31 and 0.22 kcal/mol, respectively. As with AHB21, convergence of MP2 results with respect to expansion of the basis set is also monotonic for CHB6.

D. IL16 Ion-Pair Data Set. For the IL16 ion-pair systems, SAPT0/jaDZ exhibits a MAE of 3.38 kcal/mol with a maximum error of 5.68 kcal/mol. The "bronze standard" *s*SAPT0/jaDZ increases the MAE to 5.20 kcal/mol with a maximum error of 8.27 kcal/mol. Therefore, in contrast to the case of AHB21, where scaling of $E^{(20)}_{\text{exch-disp}}(S^2)$ reduces the MAE from 2.01 and 1.58 kcal/mol, for IL16 *s*SAPT0 does not afford good error cancellation, and errors remain large. The silver standard of SAPT, SAPT2+/aDZ, performs much better, with a MAE of 0.62 kcal/mol and a maximum error of 1.87 kcal/mol.

Errors in high-level SAPT methods, with and without including the δMP2 correction, for the IL16 data set are shown in Table 6. By using CCD amplitudes for the dispersion corrections, errors in SAPT methods without δMP2 are reduced, while errors in SAPT methods with δMP2 are increased. The δMP2 term worsens the performance of SAPT2+(3) and SAPT2+(3)(CCD); however, it improves the performance of the rest of the high-level SAPT methods. The best method for these ion-pair systems is SAPT2+3-δMP2, with a MAE of 0.33 kcal/mol. The gold standard SAPT2+(3)-δMP2 gives a MAE of 0.92 kcal/mol, almost three times worse than SAPT2+3-δMP2. The extra coupling terms between induction and dispersion in SAPT2+3 as compared to SAPT2+(3) are important in ion-pair complexes. The best SAPT method for the AHB21 data set, SAPT2+(CCD)-δMP2/aTZ, performs reasonably well, with a MAE of 0.44 kcal/mol.

Table 6. Mean Absolute Errors[a] (MAEs) and Maximum Errors in SAPT Binding Energies for the IL16 Data Set

	error ($kcal\ mol^{-1}$)			
	without δMP2[b]		with δMP2[c]	
method	MAE	max	MAE	max
SAPT2+	1.01	1.95	0.34	1.74
SAPT2+(3)	0.50	1.00	0.92	2.86
SAPT2+3	1.22	2.40	0.33	0.94
SAPT2+(CCD)	0.71	1.51	0.44	2.41
SAPT2+(3)(CCD)	0.43	0.95	1.24	3.53
SAPT2+3(CCD)	0.89	1.73	0.37	1.60

[a] With respect to CCSD(T)/CBS benchmarks. [b] ${}^{t}E^{(22)}_{\text{exch-ind}}$ is scaled by $p_{\text{ex}}(\alpha = 2)$, $E^{(20)}_{\text{exch-ind}}$ is corrected by δHF, and $E^{(20)}_{\text{exch-disp}}$ is evaluated using the SEA. [c] $E^{(20)}_{\text{exch-ind}}$ is corrected by δHF, and both ${}^{t}E^{(22)}_{\text{exch-ind}}$ and $E^{(20)}_{\text{exch-disp}}$ are corrected by δMP2.

The scaled-exchange and δMP2 corrections are plotted in Figure 3c for the IL16 data set. The average contributions of $[p_{\text{ex}}(\alpha = 2)-1]\ E^{(20)}_{\text{exch-ind,resp}}$, $[p_{\text{ex}}(\alpha = 2)-1]\ {}^{t}E^{(22)}_{\text{exch-ind}}$, and δMP2 are 1.10, 0.12, and 1.22 kcal/mol, respectively. For comparison, the same three values for AHB21 are 0.99, 0.10, and 1.13 kcal/mol, respectively, that is, basically comparable if slightly smaller. (Note that the average binding energy in AHB21 is −22.49 kcal/mol, whereas in IL16, it is −109.05 kcal/mol.) We take this as an indication that the anion exerts greater influence on the magnitude of these values than does the cation.

The performance of DFT-SAPT, DFT, and MP2-based methods for IL16 is summarized in Table 7. Among these

Table 7. Mean Absolute Errors[a] (MAEs) and Maximum Errors in Binding Energies for the IL16 Data Set

	error (kcal mol^{-1})		
		maximum	
method	MAE	value	system
SAPT2+3-δMP2/aTZ[b]	0.33	0.94	IL-008
DFT-SAPT[c]/aDZ	3.57	4.80	IL-150
DFT-SAPT[c]/aTZ	2.18	3.67	IL-150
M06-2X/aTZ	0.47	0.95	IL-152
LC-VV10/aTZ	0.29	0.85	IL-144
ωB97X-D/aTZ	1.31	3.05	IL-008
ωB97X-D3/aTZ	0.89	2.32	IL-008
ωB97X-V/aTZ	0.79	1.31	IL-187
B97M-V/aTZ	0.43	1.06	IL-148
att-MP2/aTZ	0.33	1.43	IL-008
MP2/aTZ	0.92	1.67	IL-008
MP2/aQZ	0.47	1.15	IL-008
MP2/CBS	0.31	0.81	IL-008

[a] With respect to CCSD(T)/CBS benchmarks. [b] Best-performing SAPT method for this data set. [c] Includes exact second-order exchange.

methods, DFT-SAPT/aTZ exhibits a rather large MAE, 2.18 kcal/mol. The M06-2X and LC-VV10 functionals perform better for IL16 than for AHB21 or CHB6 data sets (MAEs <0.5 kcal/mol), which seems odd given the larger binding energies for IL16, whereas ωB97X-D, ωB97X-D3, and ωB97X-V (MAEs of 0.8−1.3 kcal/mol) exhibit larger errors for IL16 than for AHB21 or CHB6. B97M-V and att-MP2 exhibit MAEs <0.5 kcal/mol for IL16 that are similar to their MAEs for AHB21, although slightly larger than their MAEs for CHB6. The MP2 method shows monotonic convergence toward the CBS limit, with a MAE for MP2/CBS of 0.31 kcal/mol.

E. Summary. Overall errors for all 43 dimers contained in AHB21, CHB6, and IL16, are listed in Table 8, as obtained using a variety of methods. The SAPT0/jaDZ and bronze standard[43] *s*SAPT0/jaDZ methods afford large errors in these dimers that involve ions, with overall MAEs of almost 3 kcal/mol. The DFT-SAPT/aTZ method affords an overall MAE of 1.43 kcal/mol, roughly consistent with its MAE of 0.92 kcal/mol that has previously been reported for neutral hydrogen-bonded systems.[43] As such, none of these three methods can be recommended for sub-kcal/mol accuracy in strongly bound complexes.

The silver standard[43] SAPT2+/aDZ and gold standard[43] SAPT2+(3)-δMP2/aTZ methods afford more moderate errors, with overall MAEs of 0.67 and 0.44 kcal/mol, respectively. The SAPT2+(CCD)-δMP2/aTZ method, which gave the smallest MAE for the AHB21 data set on its own, affords an MAE of 0.44 kcal/mol for this composite data set, while the best method for IL16 on its own (SAPT2+3-δMP2/aTZ) provides a similar MAE of 0.43 kcal/mol for the composite set. These methods therefore appear to be accurate and consistent for complexes involving ions.

The SAPT2+(CCD)-δMP2/aTZ method affords MAEs of 0.28, 1.00, and 0.44 kcal/mol for the AHB21, CHB6, and IL16 data sets, respectively, whereas the MAEs engendered by SAPT2+3-δMP2/aTZ are 0.49, 0.49, and 0.33 kcal/mol, respectively. The latter method therefore offers the more consistent accuracy across different charge states. The performance of SAPT2+3-δMP2/aTZ is also quite good for neutral complexes;[43] hence, this level of theory is recommended for high-accuracy SAPT calculations in ionic complexes.

Table 8. Overall Mean Absolute Errors[a] (MAEs) and Maximum Errors in Binding Energies for the Composite AHB21 + CHB6 + IL16 Data Set[b]

	error (kcal mol^{-1})		
		maximum	
method	MAE	value	system
SAPT0/jaDZ	2.60	9.54	F^-(HF)
*s*SAPT0/jaDZ	3.15	8.27	IL-227
SAPT2+/aDZ	0.84	2.78	Cl^-(HCl)
SAPT2+(3)-δMP2/aTZ	0.67	2.96	F^-(HF)
SAPT2+(CCD)-δMP2/aTZ	0.44	2.41	IL-008
SAPT2+3-δMP2/aTZ	0.43	2.58	F^-(HF)
DFT-SAPT[c]/aTZ	1.43	6.15	Cl^-(HCl)
M06-2X/aTZ	0.88	3.97	F^-(HF)
LC-VV10/aTZ	0.91	4.60	$Li^+(C_6H_6)$
ωB97X-D/aTZ	0.73	3.05	IL-008
ωB97X-D3/aTZ	0.69	2.32	IL-008
ωB97X-V/aTZ	0.55	2.25	$Li^+(C_6H_6)$
B97M-V/aTZ	0.42	1.55	$K^+(C_6H_6)$
att-MP2/aTZ	0.47	2.47	Cl^-(HCl)
MP2/aTZ	0.79	1.96	F^-(HF)
MP2/aQZ	0.44	1.88	Cl^-(HCl)
MP2/CBS	0.34	2.64	Cl^-(HCl)

[a] With respect to CCSD(T)/CBS benchmarks. [b] For the alkali atoms in CHB6, the def2-SVP (aDZ), def2-TZVPP (aTZ), and def2-QZVPP (aQZ) basis sets are used. [c] Includes exact second-order exchange.

Among DFT methods, the newly developed ωB97X-V and B97M-V functionals afford small overall MAEs of 0.55 and 0.42 kcal/mol, respectively. Furthermore, B97M-V has the smallest maximum error among all methods used in this work, including SAPT- and MP2-based approaches. Thus, B97M-V offers accurate binding energies for both neutral[87] and ionic systems. The att-MP2/aTZ is superior to MP2/aTZ and MP2/aQZ, and it is also recommended as an efficient method to study binding energies for both neutral[47] and ionic systems. The best method for ionic systems in this work is MP2/CBS with a MAE of 0.34 kcal/mol, although large basis sets are required to eliminate BSSE. Moreover, MP2/CBS succeeds here due to the importance of electrostatics; in systems where dispersion is more important, this method is less accurate.[66,92]

IV. CONCLUSIONS

In this work, we assembled three data sets of noncovalent dimers in which one or both partners is an ion and reported benchmark CCSD(T)/CBS results for these dimers. We call these data sets AHB21 (consisting of 21 strongly hydrogen-bonded anion−neutral complexes), CHB6 (containing six cation−neutral dimers), and IL16 (composed of 16 cation−anion dimers composed of common ions found in ionic liquids).

We have systematically evaluated the accuracy of the so-called “S^2” or single-exchange approximation that is used in the first-order exchange, second-order exchange−induction, and second-order exchange−dispersion energy components. The accuracy of various levels of SAPT has been evaluated for these three data sets, and in addition, the accuracy of some DFT and MP2 methods has been assessed as well. Our findings are summarized below.

(1) For these data sets, the first-order exchange and second-order exchange−induction components are underestimated within the SEA, whereas the second-order exchange−dispersion

component is overestimated. This is consistent with previous conclusions for neutral molecules and selected ions.[44,45]

(2) For the complexes in AHB21 and IL16, the $E^{(10)}_{\text{exch}}(S^2)$ and $E^{(20)}_{\text{exch-ind,resp}}(S^2)$ terms exhibit large errors, whereas the $E^{(20)}_{\text{exch-disp}}(S^2)$ and ${}^{t}E^{(22)}_{\text{exch-ind}}(S^2)$ terms are quite accurate as compared to exact (non-SEA) results. *Ad hoc* scaling, based upon the ratio between $E^{(10)}_{\text{exch}}$ with and without the SEA [$p_{\text{ex}}(\alpha = 2)$ in eq 5], can be used to correct the deficiency in $E^{(20)}_{\text{exch-ind,resp}}(S^2)$ and thereby reduce the MAE for AHB21 from 1.0 to 0.1 kcal/mol, and the MAE for IL16 from 1.5 to 0.1 kcal/mol, as compared to the exact value of $E^{(20)}_{\text{exch-ind,resp}}$.

(3) For cations (CHB6 data set), the S^2 approximation is quite accurate.

(4) The error engendered by the SEA in the $E^{(20)}_{\text{exch-ind,resp}}$ and $E^{(30)}_{\text{exch-ind,resp}}$ terms can be compensated by the addition of the δHF correction. The δMP2 correction, defined as the difference between $E^{\text{MP2}}_{\text{int}}$ and $E^{\text{SAPT2}}_{\text{int}}$ (eq 12), can compensate for the SEA in $E^{(20)}_{\text{exch-disp}}$ and ${}^{t}E^{(22)}_{\text{exch-ind}}$.

(5) The δMP2 correction is large for anions and ion-pairs but smaller for cations. This is due primarily to the fact that the higher-order induction−dispersion coupling terms are large where anions are involved, and these terms are captured by the δMP2 correction.

(6) The magnitudes of the exchange-scaling correction, $[p_{\text{ex}}(\alpha)-1]\ E^{(20)}_{\text{exch-ind,resp}}$, and the δMP2 correction, point to the breakdown of the perturbation expansion and thus indicate cases where the individual SAPT energy components may no longer be reliable. However, total binding energies may still be accurately reproduced by SAPT methods, if the δHF and δMP2 corrections are included.

(7) For the anions in AHB21, the "gold", "silver", and "bronze standards" of wave function-based SAPT[43] [i.e., SAPT2+(3)-δMP2/aTZ, SAPT2+/aDZ, and *s*SAPT0/jaDZ, respectively] afford MAEs of 0.45, 0.77, and 1.58 kcal/mol, respectively.

(8) The best SAPT method for the AHB21 anions is SAPT2+(CCD)-δMP2/aTZ, which exhibits a MAE of 0.28 kcal/mol and a maximum error of 0.71 kcal/mol. This method is equivalent to a supermolecular MP2 calculation with dispersion corrections that employ CCD amplitudes and is therefore also known as MP2(CCD). The MP2(CCD) method performs better than the regular MP2/aTZ method with a MAE of 0.67 kcal/mol since dispersion corrections based on CCD amplitudes have been included in MP2(CCD). This method also performs well for describing hydrogen bonds between neutral monomers[43] and is recommended in cases where a balanced description of both neutral and anionic systems is required.

(9) For the CHB6 data set, the "gold" and "silver" SAPT standards[43] afford MAEs of 0.73 and 1.64 kcal/mol, respectively.

(10) The best SAPT method for the CHB6 data set is SAPT2+3-δMP2/aQZ, with a MAE of 0.2 kcal/mol and a maximum error of 0.4 kcal/mol. We recommend the use of the highest level of SAPT available, combined with the largest feasible basis set, for cation-binding calculations.

(11) For the ion pairs in IL16, the "gold", "silver", and "bronze standards" of wave function-based SAPT[43] [i.e., SAPT2+(3)-δMP2/aTZ, SAPT2+/aDZ, and *s*SAPT0/jaDZ, respectively] afford MAEs of 0.92, 0.62, and 5.20 kcal/mol, respectively. Thus, the "silver standard" performs slightly better than the "gold standard" for ion pairs.

(12) The best SAPT method for the IL16 ion pairs is SAPT2+3-δMP2/aTZ, which affords a MAE of 0.33 kcal/mol and a maximum error of 0.94 kcal/mol.

(13) The extra coupling terms between induction and dispersion in SAPT2+3 as compared to SAPT2+(3) are essential to generate good binding energies in cation-binding and ion-pair complexes.

(14) The SAPT2+(CCD)-δMP2/aTZ method affords MAEs of 0.28, 1.00, and 0.44 kcal/mol for the AHB21, CHB6, and IL16 data sets, respectively. Combining these three data sets, the overall MAE is 0.44 kcal/mol. The corresponding MAEs for SAPT2+3-δMP2/aTZ is 0.49, 0.49, and 0.33 kcal/mol, respectively, with an overall MAE of 0.43 kcal/mol. Although SAPT2+(CCD)-δMP2/aTZ is quite accurate for anionic systems, SAPT2+3-δMP2/aTZ provides a more balanced description for a variety of ionic systems. Furthermore, the overall performance of SAPT2+3-δMP2/aTZ is better than the aforementioned "gold standard" SAPT2+(3)-δMP2/aTZ method, with a MAE of 0.67 kcal/mol. Hence, we put forward the SAPT2+3-δMP2/aTZ approach as an alternative "gold standard" for ionic complexes.

(15) SAPT methods can succeed in strongly bound systems, so long as the supersystem δHF correction (eq 3 or 11) and the supersystem δMP2 correction [eq 12] are applied. These are no longer "pure" SAPT approaches, however, as they require supermolecular HF and MP2 calculations, and the decomposition into energy components may therefore become problematic.

(16) The overall MAEs for SAPT0/jaDZ, bronze standard *s*SAPT0/jaDZ, and DFT-SAPT/aTZ are 2.60, 3.15, and 1.43 kcal/mol, respectively. It is not recommended to apply these approaches to strongly-bound complexes. The performance of the silver standard SAPT2+/aDZ approach is slightly better, with an overall MAE of 0.84 kcal/mol for the three data sets considered here.

(17) Among all supermolecular methods, B97M-V/aTZ is the best DFT method with an overall MAE of 0.42 kcal/mol. MP2/CBS is the best wave function method for these ionic complexes, with an overall MAE of 0.34 kcal/mol.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Structures of the complexes in AHB21, CHB6, and IL16 data sets; raw data for binding energies computed at various levels of theory; further analysis of the S^2 and δMP2 corrections in other basis sets; and exchange-scaling results with different values of α. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*(G.J.) E-mail: georg.jansen@uni-due.de.
*(J.M.H.) E-mail: herbert@chemistry.ohio-state.edu.

Funding

Work by K.U.L. and J.M.H. was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under Award No. DE-SC0008550. Calculations by these two authors were performed at the Ohio Supercomputer Center under project PAA-0003. J.M.H. is a Camille Dreyfus Teacher-Scholar.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Kaplan, I. G. *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials*; John Wiley and Sons, Ltd: Chichester, U.K., 2006.

(2) Müller-Dethlefs, K.; Hobza, P. *Chem. Rev.* **2000**, *100*, 143−167.

(3) Riley, K. E.; Pitoňák, M.; Jurečka, P.; Hobza, P. *Chem. Rev.* **2010**, *110*, 5023−5063.

(4) Řezáč, J.; Hobza, P. *J. Chem. Theory Comput.* **2013**, *9*, 2151−2155.

(5) Šimová, L.; Řezáč, J.; Hobza, P. *J. Chem. Theory Comput.* **2013**, *9*, 3420−3428.

(6) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

(7) Grimme, S. *WIREs Comput. Mol. Sci.* **2011**, *1*, 211−228.

(8) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401:1−4.

(9) Lee, K.; Murray, É D.; Kong, L.; Lundqvist, B. I.; Langreth, D. C. *Phys. Rev. B* **2010**, *82*, 081101:1−4.

(10) Vydrov, O. A.; van Voorhis, T. *Phys. Rev. Lett.* **2009**, *103*, 063004:1−4.

(11) Vydrov, O. A.; van Voorhis, T. *J. Chem. Phys.* **2010**, *133*, 244103:1−9.

(12) Heßelmann, A. *J. Chem. Theory Comput.* **2013**, *9*, 273−283.

(13) Jeziorski, B.; Moszynski, R.; Ratkiewicz, A.; Rybak, S.; Szalewicz, K.; Williams, H. L. In *Methods and Techniques in Computational Chemistry: METECC-94*; Clementi, E., Ed.; STEF: Cagliari, Italy, 1993; Chapter 3, Vol. *B*, pp 79−129.

(14) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887−1930.

(15) Szalewicz, K.; Patkowski, K.; Jeziorski, B. In *Intermolecular Forces and Clusters II*; Wales, D. J., Ed.; Springer-Verlag: Berlin, 2005; Vol. *116*, Structure and Bonding, pp 43−117.

(16) Szalewicz, K. *WIREs Comput. Mol. Sci.* **2012**, *2*, 254−272.

(17) Hohenstein, E. G.; Sherrill, C. D. *WIREs Comput. Mol. Sci.* **2012**, *2*, 304−326.

(18) Jansen, G. *WIREs Comput. Mol. Sci.* **2014**, *4*, 127−144.

(19) Rybak, S.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1991**, *95*, 6576−6601.

(20) Moszynski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1994**, *100*, 1312−1325.

(21) Williams, H. L.; Mas, E. M.; Szalewicz, K.; Jeziorski, B. *J. Chem. Phys.* **1995**, *103*, 7374−7391.

(22) Korona, T. *J. Chem. Phys.* **2008**, *128*, 224104:1−14.

(23) Korona, T. *Phys. Chem. Chem. Phys.* **2009**, *10*, 6509−6519.

(24) Korona, T. *J. Chem. Theory Comput.* **2009**, *5*, 2663−2678.

(25) Hohenstein, E. G.; Sherrill, C. D. *J. Chem. Phys.* **2010**, *132*, 184111:1−10.

(26) Hohenstein, E. G.; Sherrill, C. D. *J. Chem. Phys.* **2010**, *133*, 014101:1−12.

(27) Hohenstein, E. G.; Sherrill, C. D. *J. Chem. Phys.* **2010**, *133*, 014107:1−7.

(28) Hohenstein, E. G.; Parrish, R. M.; Sherrill, C. D.; Turney, J. M.; Schaefer, H. F., III *J. Chem. Phys.* **2011**, *135*, 174107:1−13.

(29) Misquitta, A. J.; Podeszwa, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **2005**, *123*, 214103:1−14.

(30) Heßelmann, A.; Jansen, G.; Schütz, M. *J. Chem. Phys.* **2005**, *122*, 014103:1−17.

(31) Misquitta, A. J.; Szalewicz, K. *Chem. Phys. Lett.* **2002**, *357*, 301−306.

(32) Heßelmann, A.; Jansen, G. *Chem. Phys. Lett.* **2002**, *357*, 464−470.

(33) Heßelmann, A.; Jansen, G. *Chem. Phys. Lett.* **2002**, *362*, 319−325.

(34) Moszynski, R.; Jeziorski, B.; Szalewicz, K. *Chem. Phys.* **1992**, *166*, 329−339.

(35) Kim, D.; Tarakeshwar, P.; Kim, K. S. *J. Phys. Chem. A* **2004**, *108*, 1250−1258.

(36) Zahn, S.; Uhlig, F.; Thar, J.; Spickermann, C.; Kirchner, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 3639−3641.

(37) Singh, N. J.; Min, S. K.; Kim, D. Y.; Kim, K. S. *J. Phys. Chem. B* **2009**, *5*, 515−529.

(38) Lao, K. U.; Herbert, J. M. *J. Phys. Chem. A* **2012**, *116*, 3042−3047.

(39) Bankiewicz, B.; Matczak, P.; Palusiak, M. *J. Phys. Chem. A* **2012**, *116*, 452−459.

(40) Matczak, P. *J. Phys. Chem. A* **2012**, *116*, 8731−8736.

(41) Ansorg, K.; Tafipolsky, M.; Engels, B. *J. Phys. Chem. B* **2013**, *117*, 10093−10102.

(42) Korona, T. *Mol. Phys.* **2013**, *111*, 3705−3715.

(43) Parker, T. M.; Burns, L. A.; Parrish, R. M.; Ryno, A. G.; Sherrill, C. D. *J. Chem. Phys.* **2014**, *140*, 094106:1−16.

(44) Schäffer, R.; Jansen, G. *Theor. Chem. Acc.* **2012**, *131*, 1235:1−10.

(45) Schäffer, R.; Jansen, G. *Mol. Phys.* **2013**, *111*, 2570−2584.

(46) Goldey, M.; Head-Gordon, M. *J. Phys. Chem. Lett.* **2012**, *3*, 3592−3598.

(47) Goldey, M.; Dutoi, A.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2013**, *15*, 15869−15875.

(48) Goldey, M.; Head-Gordon, M. *J. Phys. Chem. B* **2014**, *118*, 6519−6525.

(49) Goldey, M.; Head-Gordon, M. *Chem. Phys. Lett.* **2014**, *608*, 249−254.

(50) Lao, K. U.; Herbert, J. M. *J. Chem. Phys.* **2013**, *139*, 034107:1−16.

(51) Lao, K. U.; Herbert, J. M. *J. Phys. Chem. A* **2015**, *119*, 235−253.

(52) Moszynski, R.; Jeziorski, B.; Ratkiewicz, A.; Rybak, S. *J. Chem. Phys.* **1993**, *99*, 8856.

(53) Moszyński, R.; Cybulski, S. M.; Chałasiński, G. *J. Chem. Phys.* **1994**, *100*, 4998−5010.

(54) Patkowski, K.; Podeszwa, R.; Szalewicz, K. *J. Phys. Chem. A* **2007**, *111*, 12822−12838.

(55) Hohenstein, E. G.; Jaeger, H. M.; Carrell, E. J.; Tschumper, G. S.; Sherrill, C. D. *J. Chem. Theory Comput.* **2011**, *7*, 2842−2851.

(56) Patkowski, K.; Szalewicz, K.; Jeziorski, B. *J. Chem. Phys.* **2006**, *125*, 154107:1−20.

(57) Patkowski, K.; Szalewicz, K.; Jeziorski, B. *Theor. Chem. Acc.* **2010**, *127*, 211−221.

(58) Papajak, E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2011**, *7*, 10−18.

(59) Williams, H. L.; Szalewicz, K.; Moszynski, R.; Jeziorski, B. *J. Chem. Phys.* **1995**, *103*, 4586−4599.

(60) Parrish, R. M.; Hohenstein, E. G.; Sherrill, C. D. *J. Chem. Phys.* **2013**, *139*, 174102:1−15.

(61) Řezác, J.; Hobza, P. *J. Chem. Theory Comput.* **2012**, *8*, 141−151.

(62) Flick, J. C.; Kosenkov, D.; Hohenstein, E. G.; Sherrill, C. D.; Slipchenko, L. V. *J. Chem. Theory Comput.* **2012**, *8*, 2835−2843.

(63) Lao, K. U.; Herbert, J. M. *J. Chem. Phys.* **2014**, *140*, 119901:1.

(64) Schah-Mohammedi, P.; Shenderovich, I. G.; Detering, C.; Limbach, H.-H.; Tolstoy, P. M.; Smirnov, S. N.; Denisov, G. S.; Golubev, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 12878−12879.

(65) Zahn, S.; MacFarlane, D. R.; Izgorodina, E. I. *Phys. Chem. Chem. Phys.* **2013**, *15*, 13664−13675.

(66) Jurečka, P.; Šponer, J.; Černý, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1985−1993.

(67) Řezác, J.; Riley, K. E.; Hobza, P. *J. Chem. Theory Comput.* **2011**, *7*, 2427−2438.

(68) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; Ghosh, D.; Goldey, M.; Horn, P. R.; Jacobson, L. D.; Kaliman, I.; Khaliullin, R. Z.; Kús, T.; Landau, A.; Liu, J.; Proynov, E. I.; Rhee, Y. M.; Richard, R. M.; Rohrdanz, M. A.; Steele, R. P.; Sundstrom, E. J.; Woodcock, H. L., III; Zimmerman, P. M.; Zuev, D.; Albrecht, B.; Alguire, E.; Austin, B.; Beran, G. J. O.; Bernard, Y. A.; Berquist, E.; Brandhorst, K.; Bravaya, K. B.; Brown, S. T.; Casanova, D.; Chang, C.-M.; Chen, Y.; Chien, S. H.; Closser, K. D.; Crittenden, D. L.; Diedenhofen, M.; DiStasio, R. A., Jr.; Dop, H.; Dutoi, A. D.; Edgar, R. G.; Fatehi, S.; Fusti-Molnar, L.; Ghysels, A.; Golubeva-Zadorozhnaya, A.; Gomes, J.; Hanson-Heine, M. W. D.; Harbach, P. H. P.; Hauser, A. W.; Hohenstein, E. G.; Holden, Z. C.; Jagau, T.-C.; Ji, H.; Kaduk, B.; Khistyaev, K.; Kim, J.; Kim, J.; King, R. A.; Klunzinger, P.; Kosenkov, D.; Kowalczyk, T.; Krauter, C. M.; Lao, K. U.; Laurent, A.; Lawler, K. V.; Levchenko, S. V.; Lin, C. Y.; Liu, F.; Livshits, E.; Lochan, R. C.; Luenser, A.; Manohar, P.; Manzer, S. F.; Mao, S.-P.; Mardirossian, N.; Marenich, A. V.; Maurer, S. A.; Mayhall, N. J.; Oana, C. M.; Olivares-Amaya, R.; O'Neill, D. P.; Parkhill, J. A.; Perrine, T. M.; Peverati, R.; Pieniazek, P. A.; Prociuk, A.; Rehn, D. R.; Rosta, E.; Russ, N. J.; Sergueev, N.; Sharada, S. M.; Sharmaa, S.; Small, D. W.; Sodt, A.; Stein, T.; Stück, D.; Su, Y.-C.; Thom, A. J. W.; Tsuchimochi, T.; Vogt, L.; Vydrov, O.; Wang, T.; Watson, M. A.; Wenzel, J.; White, A.; Williams, C. F.; Vanovschi, V.; Yeganeh, S.; Yost, S. R.; You, Z.-Q.; Zhang, I. Y.;

Zhang, X.; Zhou, Y.; Brooks, B. R.; Chan, G. K. L.; Chipman, D. M.; Cramer, C. J.; Goddard, W. A., III; Gordon, M. S.; Hehre, W. J.; Klamt, A.; Schaefer, H. F., III; Schmidt, M. W.; Sherrill, C. D.; Truhlar, D. G.; Warshel, A.; Xua, X.; Aspuru-Guzik, A.; Baer, R.; Bell, A. T.; Besley, N. A.; Chai, J.-D.; Dreuw, A.; Dunietz, B. D.; Furlani, T. R.; Gwaltney, S. R.; Hsu, C.-P.; Jung, Y.; Kong, J.; Lambrecht, D. S.; Liang, W.; Ochsenfeld, C.; Rassolov, V. A.; Slipchenko, L. V.; Subotnik, J. E.; van Voorhis, T.; Herbert, J. M.; Krylov, A. I.; Gill, P. M. W.; Head-Gordon, M. *Mol. Phys.* **2015**, *113*, 184−215.

(69) Turney, J. M.; Simmonett, A. C.; Parrish, R. M.; Hohenstein, E. G.; Evangelista, F.; Fermann, J. T.; Mintz, B. J.; Burns, L. A.; Wilke, J. J.; Abrams, M. L.; Russ, N. J.; Leininger, M. L.; Janssen, C. L.; Seidl, E. T.; Allen, W. D.; Schaefer, H. F.; King, R. A.; Valeev, E. F.; Sherrill, C. D.; Crawford, T. D. *WIREs Comput. Mol. Sci.* **2012**, *2*, 556−565.

(70) Neese, F. *WIREs Comput. Mol. Sci.* **2012**, *2*, 73−78.

(71) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. *WIREs Comput. Mol. Sci.* **2012**, *2*, 242−253.

(72) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243−252.

(73) Valeev, E. *Chem. Phys. Lett.* **2004**, *395*, 190−195.

(74) Bischoff, F. A.; Wolfsegger, S.; Tew, D. P.; Klopper, W. *Mol. Phys.* **2009**, *107*, 963−975.

(75) Adler, T. B.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2007**, *127*, 221106:1−4.

(76) Noga, J.; Šimunek, J. *Chem. Phys.* **2009**, *356*, 1−6.

(77) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(78) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796−6806.

(79) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.

(80) Heßelmann, A.; Korona, T. *J. Chem. Phys.* **2014**, *141*, 094107:1−17.

(81) Gross, E. K. U.; Dobson, J. F.; Petersilka, M. *Topics Curr. Chem.* **1996**, *181*, 81−172.

(82) Grüning, M.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Chem. Phys.* **2001**, *114*, 652−660.

(83) Lee, D.; Burke, K. *Mol. Phys.* **2010**, *108*, 2687−2701.

(84) Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.

(85) Lin, Y.-S.; Li, G.-D.; Mao, S.-P.; Chai, J.-D. *J. Chem. Theory Comput.* **2013**, *9*, 263−272.

(86) Mardirossian, N.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9904−9924.

(87) Mardirossian, N.; Head-Gordon, M. *J. Chem. Phys.* **2015**, *142*, 074111:1−32.

(88) Mardirossian, N.; Lambrecht, D. S.; McCaslin, L.; Xantheas, S. S.; Head-Gordon, M. *J. Chem. Theory Comput.* **2013**, *9*, 1368−1380.

(89) Dutoi, A. D.; Head-Gordon, M. *J. Phys. Chem. A* **2008**, *112*, 2110−2119.

(90) Podeszwa, R.; Bukowski, R.; Szalewicz, K. *J. Chem. Theory Comput.* **2006**, *2*, 400−412.

(91) Burns, L. A.; Vázquez-Mayagoitia, Á.; Sumpter, B. G.; Sherrill, C. D. *J. Chem. Phys.* **2011**, *134*, 084107:1−25.

(92) Cremer, D. *WIREs Comput. Mol. Sci.* **2011**, *1*, 509−530.