

# Symmetry-adapted perturbation theory with Kohn-Sham orbitals using non-empirically tuned, long-range-corrected density functionals

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The performance of second-order symmetry-adapted perturbation theory (SAPT) calculations using Kohn-Sham (KS) orbitals is evaluated against benchmark results for intermolecular interactions. Unlike previous studies of this “SAPT(KS)” methodology, the present study uses non-empirically tuned long-range corrected (LRC) functionals for the monomers. The proper  $v_{xc}(r) \rightarrow 0$  asymptotic limit is achieved by tuning the range separation parameter in order to satisfy the condition that the highest occupied KS energy level equals minus the molecule’s ionization energy, for each monomer unit. Tests for He<sub>2</sub>, Ne<sub>2</sub>, and the S22 and S66 data sets reveal that this condition is important for accurate prediction of the non-dispersion components of the energy, although errors in SAPT(KS) dispersion energies remain unacceptably large. In conjunction with an empirical dispersion potential, however, the SAPT(KS) method affords good results for S22 and S66, and also accurately predicts the whole potential energy curve for the sandwich isomer of the benzene dimer. Tuned LRC functionals represent an attractive alternative to other asymptotic corrections that have been employed in density-functional-based SAPT calculations, and we recommend the use of tuned LRC functionals in both coupled-perturbed SAPT(DFT) calculations and dispersion-corrected SAPT(KS) calculations. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4862644>]

## I. INTRODUCTION

Symmetry-adapted perturbation theory<sup>1–5</sup> (SAPT) is a popular method to calculate dimer interaction energies and to decompose them into physically meaningful components: electrostatics, induction, dispersion, and their exchange counterparts. In this approach, the Hamiltonian is partitioned into monomer Fock operators, Møller-Plesset fluctuation operators (representing intramolecular electron correlation), and the intermolecular interaction operators. Unfortunately, high-order terms in the fluctuation potentials are required in order to achieve highly accurate interaction energies, which limits the application of SAPT to dimers composed of small monomer units, or to semi-quantitative results if intramolecular electron correlation is neglected. As such, there has been considerable interest in combining the wave-function-based SAPT formalism with a low-cost density functional theory (DFT) description of the monomers, which would therefore include intramolecular electron correlation.<sup>4,5</sup>

Such a hybrid approach was first tested in 2001,<sup>6</sup> simply by substituting Kohn-Sham (KS) orbitals and energies levels into the SAPT formalism, without further justification. (Some formal properties of this approach were considered a short time later.<sup>7</sup>) This approach, wherein the KS determinant is used as the reference state for an otherwise traditional SAPT calculation, is known as SAPT(KS), and its computational cost is essentially the same as the Hartree-Fock-based approach. (The traditional second-order approach with Hartree-Fock determinants is usually called SAPT0.<sup>3</sup>) Results obtained using SAPT(KS) were disappointing,<sup>6,7</sup> however, which was ultimately attributed to the incorrect

asymptotic behavior of the exchange-correlation (XC) potential,  $v_{xc}$ , in existing density-functional approximations.<sup>6,8</sup>

The proper asymptotic behavior of  $v_{xc}$  should be<sup>9</sup>

$$v_{xc}(r) \sim -\frac{1}{r} + \Delta_{\infty} \quad (1)$$

for large  $r$ . The limiting value of  $v_{xc}(r)$  as  $r \rightarrow \infty$  should be<sup>9,10</sup>

$$\Delta_{\infty} = \text{IP} + \varepsilon_{\text{HOMO}}, \quad (2)$$

where IP is the lowest ionization potential and  $\varepsilon_{\text{HOMO}}$  is the KS eigenvalue for the highest occupied molecular orbital (HOMO). It was later demonstrated that SAPT(KS) based on an asymptotically-corrected XC functional is able to predict the electrostatics, first-order exchange, second-order induction, and exchange-induction energies with good accuracy, but second-order dispersion and exchange-dispersion energies remain quite poor.<sup>8,11,12</sup>

Accurate dispersion and exchange-dispersion energies were ultimately obtained by replacing the MP2-like sum-over-states dispersion formula (“uncoupled Hartree-Fock” approximation<sup>13</sup>) with a formula involving frequency-dependent density susceptibilities for the monomers obtained from time-dependent coupled Kohn-Sham (TD-CKS) calculations.<sup>14,15</sup> This method has variously been called DFT-SAPT or SAPT(DFT).<sup>4,5,16–19</sup> To address the issue of the long-range behavior of  $v_{xc}$ , two asymptotic correction (AC) schemes have been employed: the Tozer-Handy splicing scheme in conjunction with the Fermi-Amaldi asymptotic potential,<sup>9</sup> and the gradient-regulated asymptotic correction with the van Leeuwen-Baerends asymptotic potential.<sup>20,21</sup> The drawback of these AC schemes is that the corrected

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XC potential,  $v_{xc}^{AC}$ , is not the functional derivative of the XC energy for any exchange-correlation functional:

$$v_{xc}^{AC} \neq \frac{\delta E_{xc}}{\delta \rho}. \quad (3)$$

Exchange-correlation potentials that are not proper functional derivatives have been called “stray” potentials. Such potentials may generate spurious forces and torques, causing potentially serious problems with geometry optimizations.<sup>22</sup> Only recently has an AC model potential with  $v_{xc}^{AC} = \delta E_{xc}/\delta \rho$  been proposed,<sup>23</sup> but this functional has not yet been tested in the context of SAPT(KS). So far, the inconsistency in Eq. (3) does not seem to cause problems in the context of SAPT(KS) calculations,<sup>24</sup> but it is necessary to resolve this issue in order to derive analytic energy gradients for the extended SAPT (XSAPT) methods developed by our group,<sup>25–29</sup> which are designed for fast calculations of non-covalent clusters.

As an alternative to traditional AC model potentials, long-range corrected (LRC) density functionals, also known as range-separated hybrid functionals, can improve the asymptotic behavior of the XC potential.<sup>30–35</sup> These functionals partition the electron–electron Coulomb operator,  $r_{12}^{-1}$ , into short-range (SR) and long-range (LR) components using the error function (erf):

$$\frac{1}{r_{12}} = \underbrace{\frac{1 - \text{erf}(\omega r_{12})}{r_{12}}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\omega r_{12})}{r_{12}}}_{\text{LR}}. \quad (4)$$

Here,  $\omega$  is an adjustable range-separation parameter that determines the length scale ( $\sim \omega^{-1}$ ) of SR Coulomb potential, and is often determined by fitting to some data set.<sup>35–38</sup> For a generalized gradient approximation (GGA) of the form

$$E_{xc} = E_c + (1 - C_{\text{HF}})E_x^{\text{GGA}} + C_{\text{HF}}E_x^{\text{HF}} \quad (5)$$

(which is technically a hybrid functional if the coefficient of Hartree-Fock exchange,  $C_{\text{HF}}$ , is different from zero), the corresponding LRC function is<sup>39</sup>

$$E_{xc}^{\text{LRC}} = E_c + (1 - C_{\text{HF}})E_x^{\text{SR,GGA}} + C_{\text{HF}}E_x^{\text{SR,HF}} + E_x^{\text{LR,HF}}. \quad (6)$$

When the electron–molecule distance is large, the functional in Eq. (6) is dominated by Hartree-Fock exchange, hence the asymptotic XC potential decays as  $\sim r^{-1}$ . As such, LRC functionals exhibit the correct asymptotic distance dependence, however they do not reproduce the proper limiting value [Eq. (1)], since  $\Delta_\infty \neq 0$ .

To correct this deficiency, Baer *et al.*<sup>40,41</sup> proposed a physically-motivated (non-empirical) “tuning” of  $\omega$ , in order to satisfy the condition

$$\varepsilon_{\text{HOMO}} = -IP, \quad (7)$$

and thus ensure that  $\Delta_\infty = 0$ . When “tuned” in this way, LRC functionals predict both fundamental gaps and excitation energies quite accurately.<sup>42–44</sup>

Recently, some conventional (statistically-optimized) LRC functionals have been used in the context of SAPT(DFT) calculations, with very poor results.<sup>24</sup> This failure is attributed to the incorrect asymptotic limit of  $v_{xc}$ , and the authors of

Ref. 24 even go so far as to suggest that the name “long-range corrected functional” is inappropriate for functionals based on Eq. (6). Actually, we had already shown that LRC functionals with standard, statistically-optimized range separation parameters do not correct the dispersion problems in SAPT(KS) calculations, although they do afford slightly better results (as compared to SAPT0) for strongly hydrogen-bonded systems.<sup>26</sup> In the present study, we will show that the aforementioned non-empirical tuning procedure, when applied in a monomer-specific way, affords SAPT(KS) energy components in good agreement with high-level benchmarks, except for this dispersion energy, which is still poor. The dispersion energy, however, can be accurately incorporated via empirical potentials, as we will demonstrate, yielding high-accuracy SAPT(KS)+D calculations where the exchange-correlation functional is well-defined [unlike the situation in Eq. (3)], and is thus appropriate for the formulation of analytic energy gradients.

## II. THEORY

The traditional second-order SAPT interaction energy (SAPT0 method<sup>3</sup>) can be written as

$$E_{\text{int,resp}}^{\text{SAPT0}} = E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)}. \quad (8)$$

The notation  $E^{(nl)}$  indicates a term that is  $n$ th order in the intermolecular interaction and  $l$ th order in the monomer fluctuation potentials, hence the  $E^{(n0)}$  energy components in Eq. (8) imply that no intramolecular electron correlation is included in SAPT0. The “response” (resp) subscripts indicate that the infinite-order response correction for induction is incorporated by solving coupled perturbed Hartree-Fock equations.<sup>45,46</sup> In SAPT(KS), the intramolecular correlation is included implicitly, so the superscript  $l$  is dropped and one has

$$E_{\text{int}}^{\text{SAPT(KS)}} = E_{\text{elst}}^{(1)}(\text{KS}) + E_{\text{exch}}^{(1)}(\text{KS}) + E_{\text{ind,resp}}^{(2)}(\text{KS}) + E_{\text{exch-ind,resp}}^{(2)}(\text{KS}) + E_{\text{disp}}^{(2)}(\text{KS}) + E_{\text{exch-disp}}^{(2)}(\text{KS}). \quad (9)$$

The computational cost of either method is about the same.

In the case of traditional (Hartree–Fock-based) SAPT methods, the induction terms using “uncoupled” and “coupled” monomer densities are identical if the infinite-order intramolecular correlation is included:<sup>47</sup>

$$\sum_{l=0}^{\infty} E_{\text{ind}}^{(2l)} = \sum_{l=0}^{\infty} E_{\text{ind,resp}}^{(2l)}. \quad (10)$$

Since intramolecular correlation is implicitly included in SAPT(KS), the difference between SAPT(KS) induction energies based on coupled versus uncoupled monomer densities is expected to be smaller than in traditional wave function-based SAPT, and the uncoupled sum-over-states formula works fairly well for the induction energy.<sup>6,8,12,48</sup> Since orbital relaxation is present in the CKS static response theory but not in the uncoupled sum-over-states formula, the CKS

method should in principle give better results for the induction energy as compared to an uncoupled calculation, at least at large intermolecular separation.<sup>48</sup> In this study, the orbital relaxation for the induction and exchange-induction energies in SAPT(KS) are approximated as the energy difference between coupled and uncoupled terms calculated by SAPT0,

$$E_{\text{ind,resp}}^{(2)}(\text{KS}) = E_{\text{ind}}^{(2)}(\text{KS}) + E_{\text{ind,resp}}^{(20)} - E_{\text{ind}}^{(20)}, \quad (11a)$$

$$E_{\text{exch-ind,resp}}^{(2)}(\text{KS}) = E_{\text{exch-ind}}^{(2)}(\text{KS}) + E_{\text{exch-ind,resp}}^{(20)} - E_{\text{exch-ind}}^{(20)}. \quad (11b)$$

Thorough comparisons to benchmark calculations, as presented below, support the accuracy and robustness of this approximation.

When truncating the perturbation series at second order, as in Eqs. (8) and (9), it is common to incorporate higher-order polarization effects by means of a correction

$$\delta E_{\text{int,resp}}^{\text{HF}} = E_{\text{int}}^{\text{HF}} - (E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)}), \quad (12)$$

where  $E_{\text{int}}^{\text{HF}}$  denotes the supermolecular (dimer) Hartree-Fock interaction energy, with counterpoise correction. The  $\delta E_{\text{int,resp}}^{\text{HF}}$  term is recommended when the monomers are polar.<sup>3,49-52</sup>

### III. COMPUTATIONAL DETAILS

To determine the usefulness of SAPT(KS) calculations using tuned LRC functionals, we will use benchmark energy components determined from high-level calculations for a variety of small dimers. High-accuracy energy components for He<sub>2</sub> and Ne<sub>2</sub> are available,<sup>24,53-55</sup> obtained using highly correlated wave functions evaluated near the complete basis set (CBS) limit. For Ne<sub>2</sub>, the best available calculations<sup>24</sup> were obtained using the SAPT(CCSD) method.<sup>56-59</sup> For He<sub>2</sub>, *exact* energy components, obtained with a complete account of electron correlation (equivalent to full configuration interaction), and with a basis set that is saturated using a Gaussian-type geminal (GTG), are available;<sup>53-55</sup> this method has been called SAPT(GTG). For the S22 data set,<sup>60</sup> benchmark energy components were computed at the SAPT2+(3)/aug-cc-pVTZ level using the Psi4 program,<sup>69</sup> and are available in the supplementary material.<sup>70</sup> [The SAPT2+(3) method includes terms beyond second order; see Ref. 3.] Total binding energies (though not the individual energy components), computed at the CCSD(T)/CBS level, are available for both the S22 and S66 data sets.<sup>62,63</sup> In addition, we will use the CCSD(T)/CBS potential energy curves for the “sandwich” ( $\pi$ -stacked) isomer of the benzene dimer, from Ref. 64.

In addition to examining the popular S22 and S66 data sets,<sup>60,65</sup> we have assembled a new set of benchmarks here. This data set, which we designate as SS41, consists of 41 small systems (dimers) taken from some existing data sets. Namely, we take the 24 dimers from the A24 data set;<sup>66</sup> the formamide and formic acid dimers from S22;<sup>60</sup> nine dimers from the S66 data set<sup>65</sup> (specifically, H<sub>2</sub>O⋯CH<sub>3</sub>OH, CH<sub>3</sub>OH⋯CH<sub>3</sub>OH, CH<sub>3</sub>OH⋯CH<sub>3</sub>NH<sub>2</sub>, CH<sub>3</sub>OH⋯H<sub>2</sub>O, CH<sub>3</sub>NH<sub>2</sub>⋯CH<sub>3</sub>OH, CH<sub>3</sub>NH<sub>2</sub>⋯CH<sub>3</sub>NH<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>⋯H<sub>2</sub>O, and two isomers

of H<sub>2</sub>O⋯CH<sub>3</sub>NH<sub>2</sub>); and finally, six dimers from the X40 data set<sup>67</sup> (specifically, CH<sub>4</sub>⋯F<sub>2</sub>, CH<sub>3</sub>F⋯CH<sub>4</sub>, CH<sub>3</sub>F⋯CH<sub>3</sub>F, HF⋯CH<sub>3</sub>OH, HF⋯CH<sub>3</sub>NH<sub>2</sub>, and CH<sub>3</sub>OH⋯CH<sub>3</sub>F). Benchmark energy components for the SS41 dimers are reported here for the first time; these were computed at the SAPT2+(3)/aug-cc-pVQZ level using MP2 natural orbital approximations to accelerate the calculations, as described in Ref. 68. These calculations were performed using the Psi4 program,<sup>69</sup> and the benchmark energy components for SS41 are available in the supplementary material.<sup>70</sup>

As in our previous work on XSAPT,<sup>27,28</sup> we will use the LRC- $\omega$ PBE<sup>71</sup> and LRC- $\omega$ PBEh<sup>38</sup> functionals for SAPT(KS) calculations. These functionals are based on the short-range  $\omega$ PBE exchange functional,<sup>33</sup> augmented with 100% long-range Hartree-Fock exchange as in Eq. (6). The LRC- $\omega$ PBEh functional also contains 20% short-range Hartree-Fock exchange ( $C_{\text{HF}} = 0.2$ ), whereas LRC- $\omega$ PBE does not ( $C_{\text{HF}} = 0$ ). Statistically-optimized values of the range separation parameter have been suggested as either  $\omega = 0.3 \text{ bohr}^{-1}$  or  $\omega = 0.4 \text{ bohr}^{-1}$  for LRC- $\omega$ PBE,<sup>71,72</sup> and  $\omega = 0.2 \text{ bohr}^{-1}$  for LRC- $\omega$ PBEh.<sup>38</sup> A previous study of LRC functionals for SAPT(DFT) calculations used LRC- $\omega$ PBE with  $\omega = 0.4 \text{ bohr}^{-1}$ .<sup>24</sup> In this work, however, the value of  $\omega$  is determined by monomer-specific tuning to satisfy Eq. (7). [Monomer-specific AC model potentials have previously been used in the context of SAPT(DFT) and DFT-SAPT,<sup>17,18</sup> but monomer-specific LRC functionals have not been used in this context.] Tuned values of  $\omega$ , for each monomer appearing in the dimers examined herein, are available in the supplementary material.<sup>70</sup>

We use the aug-cc-pV6Z and aug-cc-pV5Z basis sets for the SAPT(KS) calculations on He<sub>2</sub> and Ne<sub>2</sub>, respectively, in order to obtain results near the CBS limit. For SAPT calculations on the SS41 data set, we use the aug-cc-pVQZ basis set. The aug-cc-pVTZ basis set was used for S22, S66, and the benzene dimer potential curve. Except for He<sub>2</sub> and Ne<sub>2</sub>, all of the total binding energies computed with SAPT methods include the  $\delta E_{\text{int,resp}}^{\text{HF}}$  correction. All SAPT calculations employ a dimer-centered basis set,<sup>73</sup> meaning that monomer wave functions were converged using the dimer’s basis set. With the exception of the two rare-gas dimers, we used the resolution-of-identity approximation (combined with standard auxiliary basis sets) to accelerate the wave function-based SAPT calculations, performed using Psi4.<sup>69</sup> SAPT(KS) calculations with the resolution-of-identity approximation were performed using a locally-modified version of Q-Chem.<sup>74,75</sup>

We will also report “SAPT(KS)+D” calculations that use an empirical dispersion potential in place of the  $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$  terms in second-order SAPT. This “+D” potential is taken from Ref. 76 and has been shown to afford good results for a wide variety of different systems.<sup>28,76</sup>

### IV. RESULTS AND DISCUSSION

He<sub>2</sub> and Ne<sub>2</sub> are popular test systems for SAPT-based methods, as they are small enough to use high-level wave function-based SAPT methods near the CBS limit. SAPT(KS) results for these two dimers, using LRC functionals, are

TABLE I. Interaction energy components for He<sub>2</sub> at its equilibrium distance (5.6 bohrs), calculated using the dimer-centered aug-cc-pV6Z basis. Values in parentheses are the percentage errors with respect to the GTG benchmarks, whereas other values are actual energies in units of cm<sup>-1</sup>.

Method	$E_{\text{elst}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$	Total
Exact <sup>a</sup>							-7.651
CCSD(T)/CBS <sup>b</sup>							-7.420
SAPT(GTG) benchmark <sup>c</sup>	-1.187	8.540	-0.196	0.177	-15.565	0.515	-7.716
LRC- $\omega$ PBE <sup>d</sup> ( $\omega = 0.3$ bohr <sup>-1</sup> )	(114.18)	(131.54)	(154.71)	(149.10)	(11.38)	(41.46)	0.565
LRC- $\omega$ PBE <sup>d</sup> (tuning $\omega$ )	(1.67)	(1.34)	(3.44)	(11.95)	(21.33)	(30.70)	-4.664
LRC- $\omega$ PBE+D <sup>d,e</sup> (tuning $\omega$ )							-7.332
LRC- $\omega$ PBEh <sup>d</sup> ( $\omega = 0.2$ bohr <sup>-1</sup> )	(70.17)	(94.22)	(112.15)	(107.25)	(5.89)	(23.49)	-1.435
LRC- $\omega$ PBEh <sup>d</sup> (tuning $\omega$ )	(0.13)	(0.30)	(1.64)	(10.30)	(20.83)	(29.74)	-4.615
LRC- $\omega$ PBEh+D <sup>d,e</sup> (tuning $\omega$ )							-7.211

<sup>a</sup>From Ref. 77.

<sup>b</sup>From Ref. 24.

<sup>c</sup>From Refs. 53–55.

<sup>d</sup>SAPT(KS) using the indicated density functional.

<sup>e</sup>SAPT(KS) using the “+D” dispersion correction from Ref. 76.

listed in Table I for He<sub>2</sub> and Table II for Ne<sub>2</sub>. Conventional (statistically-optimized) LRC functionals, by which we mean LRC- $\omega$ PBE with  $\omega = 0.3$  bohr<sup>-1</sup> and LRC- $\omega$ PBEh with  $\omega = 0.2$  bohr<sup>-1</sup>, afford large errors for all of the energy components. For example, the error in  $E_{\text{ind}}^{(2)}$  using LRC- $\omega$ PBE (with  $\omega = 0.3$  bohr<sup>-1</sup>) is about 150%. The tuning strategy, on the other hand, reduces errors in  $E_{\text{elst}}^{(1)}$ ,  $E_{\text{exch}}^{(1)}$ ,  $E_{\text{ind}}^{(2)}$ , and  $E_{\text{exch-ind}}^{(2)}$  to just a few percent. In the case of the dispersion interaction, the tuning strategy improves the results for Ne<sub>2</sub> but has deleterious effects for He<sub>2</sub>. Previous studies have found that SAPT(KS), using the standard second-order, uncoupled dispersion formula, afford poor dispersion energies even if AC functionals are employed.<sup>14,15</sup> This observation is consistent with the results presented here.

SAPT(KS) dispersion energies can be greatly improved by computing frequency-dependent density susceptibilities for the monomers and then evaluating the dispersion energy using a generalized Casimir-Polder formalism.<sup>14,15,18</sup> The cost of such a calculation, however, scales no better than  $\mathcal{O}(N^5)$  with respect to monomer size.<sup>78</sup> Alternatively, one can use an empirical dispersion potential designed for SAPT to obtain the dispersion energy,<sup>8,76,79,80</sup> Here, we report dispersion-corrected SAPT(KS)+D results using the

empirical dispersion potential from Ref. 76 in conjunction with tuned LRC functionals.

The  $E_{\text{elst}}^{(1)}$ ,  $E_{\text{exch}}^{(1)}$ ,  $E_{\text{ind}}^{(2)}$ , and  $E_{\text{exch-ind}}^{(2)}$  terms calculated by SAPT(KS) with AC XC potentials, plus an empirical dispersion potential, constitutes an approach that has been called SAPT(KS)+D.<sup>8,76,80</sup> Here, we apply this method not with AC model potentials but rather with LRC functionals. For He<sub>2</sub>, SAPT(KS)+D gives very good results for the total binding energy, although errors are slightly larger for Ne<sub>2</sub>. Because the SAPT(KS) method affords good results for the energy components  $E_{\text{elst}}^{(1)}$ ,  $E_{\text{exch}}^{(1)}$ ,  $E_{\text{ind}}^{(2)}$ , and  $E_{\text{exch-ind}}^{(2)}$  in both rare-gas dimers, it seems that the problem lies with the empirical dispersion potential. The dispersion energy in SAPT calculations converges very slowly as a function of the one-particle basis set,<sup>81</sup> thus the parameters in the “+D” potential of Ref. 76 are fit to dispersion energies for a training set of dimers computed at the SAPT(DFT) level using the aug-cc-pVTZ basis set with additional mid-bond functions. It is possible that this basis is insufficient to afford converged dispersion energies for the Ne<sub>2</sub> system. We note that SAPT(KS)+D results of similar accuracy to those reported here can be obtained with AC model potentials,<sup>8,48,80</sup> but at the cost of sacrificing the relationship between  $v_{\text{xc}}$  and  $E_{\text{xc}}$ .

TABLE II. Interaction energy components for Ne<sub>2</sub> at its equilibrium distance (3.1 Å), calculated using the dimer-centered aug-cc-pV5Z basis. Values in parentheses are the percentage errors with respect to the SAPT(CCSD) benchmarks, whereas other values are actual energies in units of cm<sup>-1</sup>.

Method	$E_{\text{elst}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$	Total
CCSD(T)/CBS <sup>a</sup>							-28.653
SAPT(CCSD)/CBS benchmark <sup>a</sup>	-8.997	36.317	-7.533	7.752	-60.318	3.187	-29.592
LRC- $\omega$ PBE <sup>b</sup> ( $\omega = 0.3$ bohr <sup>-1</sup> )	(89.82)	(89.73)	(120.48)	(120.26)	(56.36)	(45.84)	-37.370
LRC- $\omega$ PBE <sup>b</sup> (tuning $\omega$ )	(4.46)	(1.63)	(9.08)	(9.84)	(30.83)	(26.61)	-48.125
LRC- $\omega$ PBE+D <sup>b,c</sup> (tuning $\omega$ )							-23.274
LRC- $\omega$ PBEh <sup>b</sup> ( $\omega = 0.2$ bohr <sup>-1</sup> )	(55.14)	(55.23)	(77.93)	(77.68)	(54.96)	(22.88)	-46.763
LRC- $\omega$ PBEh <sup>b</sup> (tuning $\omega$ )	(1.99)	(3.62)	(5.45)	(6.20)	(32.00)	(24.66)	-48.256
LRC- $\omega$ PBEh+D <sup>b,c</sup> (tuning $\omega$ )							-22.762

<sup>a</sup>From Ref. 24.

<sup>b</sup>SAPT(KS) using the indicated density functional.

<sup>c</sup>SAPT(KS) using the “+D” dispersion correction from Ref. 76.



TABLE III. Mean unsigned errors (MUEs), in kcal/mol, and percent errors (in parentheses), for interaction energy components of SS41 data set, with respect to benchmarks computed at the SAPT2+(3)/aug-cc-pVQZ level. The errors in total binding energies are with respect to CCSD(T)/CBS results.<sup>62,63,66,67</sup> The  $\delta E_{\text{int,resp}}^{\text{HF}}$  correction is added to the total binding energies of the SAPT calculations.

Method	$E_{\text{elst}}^{(1)}$	$E_{\text{exch}}^{(1)}$	$E_{\text{ind}}^{(2)}$	$E_{\text{exch-ind}}^{(2)}$	$E_{\text{disp}}^{(2)}$	$E_{\text{exch-disp}}^{(2)}$	Total
SAPT2+(3) <sup>a</sup>							0.14 (4.97)
LRC- $\omega$ PBE <sup>a,b</sup>	0.12 (4.37)	0.20 (4.33)	0.09 (3.59)	0.14 (7.25)	0.23 (6.65)	0.09 (15.93)	0.22 (10.93)
LRC- $\omega$ PBEh <sup>a,b</sup>	0.08 (4.44)	0.16 (3.27)	0.06 (2.52)	0.10 (5.50)	0.22 (6.73)	0.08 (14.41)	0.34 (13.29)
SAPT0 <sup>a</sup>	0.26 (9.04)	0.70 (9.09)	0.33 (9.56)	0.19 (9.56)	0.24 (7.37)	0.00 <sup>c</sup> (0.00) <sup>c</sup>	0.69 (13.53)

<sup>a</sup>aug-cc-pVQZ basis set.

<sup>b</sup>SAPT(KS) results using the indicated density functional and tuning  $\omega$ .

<sup>c</sup>SAPT0 and SAPT2+(3) share the same formula for  $E_{\text{exch-disp}}^{(2)}$ .

Turning now to larger systems, in Table III we present the mean unsigned errors (MUEs) and mean unsigned percentage errors (MUPEs) for SAPT(KS) and SAPT0 calculations of the SS41 data set, as compared to benchmark energy components computed at the SAPT2+(3)/aug-cc-pVQZ level. Once again, SAPT(KS) with tuned LRC functionals gives very good results for the non-dispersion energy components and is much better than the SAPT0 results where the intramolecular electron correlation is completely neglected. At the SAPT0 level, errors in total binding energies range up to 5.4 kcal/mol, with the largest (absolute) error obtained for the doubly hydrogen-bonded formic acid dimer, a system where intramolecular electron correlation is known to have a large effect on the binding energy.<sup>82</sup>

Surprisingly, SAPT(KS) also gives quite good results for dispersion components and total binding energies for the SS41 data set. As proposed by Hobza and co-workers,<sup>83</sup> a complex should be considered to be dominated by electrostatics if the electrostatic component ( $E_{\text{elst}}^{(1)}$ ) is at least twice as large as the dispersion component ( $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$ ), and *vice versa* for a dispersion-dominated complex. Otherwise, the complex is classified as having interactions of mixed type. According to this classification scheme, the SS41 data set contains 16 electrostatically-dominated complexes, 12 dispersion-dominated complexes, and 13 mixed-type complexes. The three largest errors (each about 20%) in SAPT(KS) dispersion components occur for the dispersion-dominated complexes, but these 20% errors only translate into  $\approx 0.5$  kcal/mol errors since the dispersion component is no larger than  $-2.4$  kcal/mol [at the SAPT2+(3)/aug-cc-pVQZ level], even for the dispersion-dominated complexes. Larger molecules with more electrons are needed in order to obtain larger dispersion energies.

The S22 and S66 data sets<sup>60,65</sup> are popular for benchmarking non-covalent interactions. [For the latest, basis-set-consistent revisions to the CCSD(T)/CBS binding energies, see Ref. 62 for S22 and Ref. 63 for S66.] These data sets contain larger molecules, as compared to SS41; the  $\pi$ -stacked adenine–thymine dimer, for example, has a dispersion interaction of about 18 kcal/mol. For S22, we calculated benchmark energy components at the SAPT2+(3)/aug-cc-pVTZ level.

These comparisons are listed in Table IV, where the electrostatic, exchange, induction, and dispersion energies are defined according to<sup>3,61</sup>

$$E_{\text{electrostatic}} = E_{\text{elst}}^{(1)}, \quad (13a)$$

$$E_{\text{exchange}} = E_{\text{exch}}^{(1)}, \quad (13b)$$

$$E_{\text{induction}} = E_{\text{ind,resp}}^{(2)} + E_{\text{exch-ind,resp}}^{(2)} + \delta E_{\text{int,resp}}^{\text{HF}}, \quad (13c)$$

$$E_{\text{dispersion}} = E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}. \quad (13d)$$

The SAPT(KS) method yields smaller errors in electrostatic, exchange, and induction energies as compared to SAPT0. This suggests that intramolecular electron correlation is important for the molecules in S22. SAPT(KS) results based on LRC- $\omega$ PBE and LRC- $\omega$ PBEh afford similar MUEs. For the dispersion energy, on the other hand, SAPT(KS) calculations afford larger errors as compared to SAPT0, in accordance with previous observations that the use of KS orbitals and eigenvalues is detrimental to the quality of the MP2-like sum-over-states dispersion energy.<sup>26</sup> The error in the dispersion energy for  $\pi$ -stacked adenine–thymine is about 16% or 3 kcal/mol.

Table V shows the MUEs for total binding energies with respect to CCSD(T)/CBS results for the S22 data set<sup>62</sup> and the

TABLE IV. Mean unsigned errors (MUEs), in kcal/mol, and percent errors (in parentheses), for individual energy components of the S22 data set, with respect to benchmarks computed at the SAPT2+(3)/aug-cc-pVTZ level. All calculations were performed at S22 geometries.

Method	Energy components							
	Electrostatic		Exchange		Induction		Dispersion	
LRC- $\omega$ PBE <sup>a,b</sup>	0.19	(3.05)	0.59	(5.65)	0.13	(3.65)	1.04	(13.90)
LRC- $\omega$ PBEh <sup>a,b</sup>	0.17	(3.46)	0.57	(5.64)	0.13	(3.28)	1.05	(13.97)
SAPT0 <sup>b</sup>	0.42	(6.47)	1.25	(8.05)	0.27	(4.49)	0.72	(9.61)

<sup>a</sup>SAPT(KS) results using the indicated density functional and tuning  $\omega$ .

<sup>b</sup>aug-cc-pVTZ basis set.

TABLE V. Mean unsigned errors (MUEs), in kcal/mol, and percent errors (in parentheses), with respect to CCSD(T)/CBS benchmarks for the S22 data set<sup>62</sup> and the S66 data set<sup>63</sup> along with subsets consisting of the hydrogen-bonded dimers, dispersion-dominated dimers, and dimers of mixed influence. All calculations were performed at S22 and S66 geometries and the  $\delta E_{\text{int,resp}}^{\text{HF}}$  corrections are added to the total binding energies of the SAPT calculations.

Method	H-bonded		Disp.-bound		Mixed		All	
—S22—								
LRC- $\omega$ PBE <sup>a,b</sup>	0.61	(3.84)	2.60	(54.74)	0.92	(25.09)	1.43	(29.11)
LRC- $\omega$ PBE+D <sup>a,b,c</sup>	0.48	(3.24)	1.33	(19.39)	0.56	(13.00)	0.82	(12.22)
LRC- $\omega$ PBEh <sup>a,b</sup>	1.22	(7.00)	2.77	(58.69)	1.13	(30.41)	1.75	(33.25)
LRC- $\omega$ PBEh+D <sup>a,b,c</sup>	0.43	(2.99)	1.53	(25.60)	0.28	(7.96)	0.78	(12.79)
SAPT0 <sup>b</sup>	2.72	(16.91)	2.00	(41.17)	1.01	(26.96)	1.91	(28.93)
SAPT0+D <sup>b,c</sup>	3.20	(21.08)	1.39	(21.50)	0.95	(23.41)	1.83	(21.98)
SAPT2+(3) <sup>b</sup>	0.51	(3.62)	0.38	(4.86)	0.12	(3.05)	0.34	(3.89)
—S66—								
LRC- $\omega$ PBE <sup>a,b</sup>	0.22	(2.18)	1.52	(43.99)	0.82	(22.99)	0.85	(23.05)
LRC- $\omega$ PBE+D <sup>a,b,c</sup>	0.32	(3.61)	0.63	(14.40)	0.35	(9.15)	0.44	(9.05)
LRC- $\omega$ PBEh <sup>a,b</sup>	0.57	(5.56)	1.66	(48.10)	1.02	(28.52)	1.09	(27.34)
LRC- $\omega$ PBEh+D <sup>a,b,c</sup>	0.21	(2.19)	0.69	(15.54)	0.45	(12.22)	0.45	(9.88)
SAPT0 <sup>b</sup>	1.52	(14.55)	1.09	(30.34)	0.89	(24.90)	1.18	(23.19)
SAPT0+D <sup>b,c</sup>	1.89	(19.25)	0.90	(21.36)	0.83	(22.69)	1.22	(21.03)

<sup>a</sup>SAPT(KS) results using the indicated density functional and tuning  $\omega$ .

<sup>b</sup>aug-cc-pVTZ basis set.

<sup>c</sup>Using the empirical dispersion potential from Ref. 76.

S66 data set.<sup>63</sup> Both sets are divided to three subsets consisting of the hydrogen-bonded complexes (which are dominated by electrostatics), the dispersion-dominated complexes, and complexes with mixed influence, according to Hobza's classification scheme,<sup>83</sup> as discussed above. The main sources of error for the SAPT(KS) calculations are in the dispersion-dominated complexes, where the MUEs are 2.6 kcal/mol (S22) and 1.5 kcal/mol (S66). Substituting the empirical dispersion potential developed by Podszwa *et al.*<sup>76</sup> in place of the SAPT(KS) dispersion energy, to obtain a SAPT(KS)+D method based on LRC functionals, the MUEs in total binding energies are reduced to 0.8 kcal/mol (S22) and 0.4 kcal/mol (S66).

It has previously been pointed out that the empirical dispersion potential developed in Ref. 76 and used here affords relatively large errors for the  $\pi$ -stacked uracil dimer and the  $\pi$ -stacked adenine–thymine complexes.<sup>28</sup> In fact,  $\pi$ -stacked complexes are underrepresented in the training set used to parameterize this potential; only the sandwich isomer of  $(\text{C}_6\text{H}_6)_2$  and the pyrazine dimer are included as examples of  $\pi$ -stacking among the 79 dimers in the training set.<sup>76</sup> For the uracil dimer, this dispersion potential overestimates the SAPT2+(3)/aug-cc-pVTZ dispersion energy by 1.5 kcal/mol, and for adenine–thymine by 1.8 kcal/mol. If we eliminate these two problematic systems from the S22 data set, then the MUE for SAPT(KS)+D using both density functionals examined here is reduced to about 0.5 kcal/mol for both the dispersion-dominated subset and the entire set of 20 complexes (S22 minus two). Similarly for S66, the MUE for SAPT(KS)+D using both functionals is reduced to 0.4 kcal/mol when the  $\pi$ -stacked uracil dimer is removed from the data set.

For the SAPT0, however, the use of the dispersion potential from Ref. 76 does not obviously improve the results

for either S22 or S66. Furthermore, the results for hydrogen-bonded complexes described at the SAPT0+D level are worse than the SAPT0 results that use the MP2-type dispersion formula. This implies that dispersion is not the only term in SAPT0 that needs improvement: intramolecular electron correlation is important as well.

Finally, we use these SAPT(KS) methods to compute the potential energy curve for the dispersion-dominated sandwich isomer of the benzene dimer, which is regarded as a stringent test of computational methods. As shown in Fig. 1, SAPT(KS) methods that use second-order MP2-type dispersion greatly overestimate the interaction energy across the whole potential energy curve. The SAPT(KS)+D methods slightly underestimate the binding energy at short intermolecular

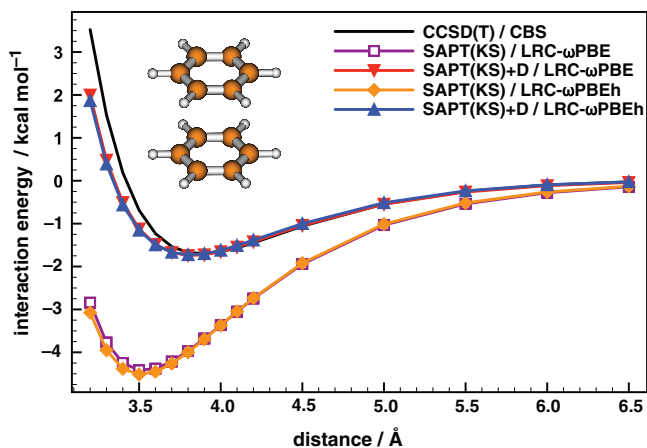


FIG. 1. Potential energy curves for the “sandwich” isomer of  $(\text{C}_6\text{H}_6)_2$  as a function of the center-to-center distance between the two benzene rings. Benchmark CCSD(T)/CBS results are taken from Ref. 64. The dimer-centered aug-cc-pVTZ basis set was used for the SAPT(KS) calculations

distance, but are very accurate beyond the minimum-energy distance.

## V. CONCLUSIONS

The increasingly-popular non-empirical tuning procedure of Baer *et al.*<sup>41</sup> for LRC (range-separated hybrid) functionals affords an XC potential with not only the correct asymptotic distance dependence, but also the correct limiting value as  $r \rightarrow \infty$ . Results presented herein demonstrate that satisfaction of this condition is very important to obtain quantitative results for the non-dispersion energy components in SAPT(KS) calculations. Although unacceptably large errors remain in the dispersion energies predicted by SAPT(KS), we expect that dispersion energies obtained from frequency-dependent density susceptibilities, computed by solving TD-CKS equations as in the SAPT(DFT) approach,<sup>16–19</sup> should yield quantitative results for the dispersion energies. Thus, LRC functionals should be useful as substitutes for AC model potentials in SAPT(DFT) and DFT-SAPT, while preserving the relationship  $v_{xc} = \delta E_{xc} / \delta \rho$  that is sacrificed when AC model potentials are employed to “graft on” correct asymptotic behavior to some existing density functional. This relationship between functional and potential is crucial where analytic gradients are needed, which is a direction that our group is headed with “XSAPT” methods.<sup>25–29</sup>

As an alternative to SAPT(DFT), in the present work we used an empirical dispersion potential<sup>76</sup> to replace the second-order dispersion energy in SAPT(KS). The resulting SAPT(KS)+D method affords quantitative binding energies for the S22 and S66 data sets, save for a couple of  $\pi$ -stacked complexes, for which we have previously argued<sup>28</sup> that re-parameterization of the dispersion potential is needed. Although “conventional” LRC functionals that employ a statistically-optimized value for the range separation parameter, which need not provide the correct limiting value of  $v_{xc}$ , have been shown to afford poor results in SAPT(DFT) calculations,<sup>24</sup> the tuning procedure used here affords good results for all energy components except dispersion, as compared to high-level SAPT2+(3) calculations.

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