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Intermolecular potentials based on symmetry-adapted perturbation theory with dispersion energies from time-dependent density-functional calculations

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Recently, three of us have proposed a method [Phys. Rev. Lett. **91**, 33201 (2003)] for an accurate calculation of the dispersion energy utilizing frequency-dependent density susceptibilities of monomers obtained from time-dependent density-functional theory (DFT). In the present paper, we report numerical calculations for the helium, neon, water, and carbon dioxide dimers and show that for a wide range of intermonomer separations, including the van der Waals and short-range repulsion regions, the method provides dispersion energies with accuracies comparable to those that can be achieved using the current most sophisticated wave-function methods. If the dispersion energy is combined with (i) the electrostatic and first-order exchange interaction energies as defined in symmetry-adapted perturbation theory (SAPT) but computed using monomer Kohn-Sham (KS) determinants, and (ii) the induction energy computed using the coupled KS static response theory, (iii) the exchange-induction and exchange-dispersion energies computed using KS orbitals and orbital energies, the resulting method, denoted by SAPT(DFT), produces very accurate total interaction potentials. For the helium dimer, the only system with nearly exact benchmark values, SAPT(DFT) reproduces the interaction energy to within about 2% at the minimum and to a similar accuracy for all other distances ranging from the strongly repulsive to the asymptotic region. For the remaining systems investigated by us, the quality of the SAPT(DFT) interaction energies is so high that these energies may actually be more accurate than the best available results obtained with wave-function techniques. At the same time, SAPT(DFT) is much more computationally efficient than any method previously used for calculating the dispersion and other interaction energy components at this level of accuracy. © 2005 American Institute of Physics.
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I. INTRODUCTION

Symmetry-adapted perturbation theory (SAPT) provides not only a conceptual basis for understanding intermolecular interactions, but also an efficient computational framework for accurate predictions of interaction energies.^{1,2} SAPT calculations can now be performed for fairly large molecules such as the dimethylnitramine dimer.³ Intermolecular force fields (potentials) for still larger systems are obviously of significant interest; however, calculations for such systems are not practical at the present since computer resources required by SAPT (or any other wave-function-based method that includes correlation effects at a level adequate for describing intermolecular interactions) scale as high powers of the system size. Density-functional theory (DFT) is much less demanding on computer resources, however, the supermolecular DFT approach is not suitable for computing interactions of systems with a significant dispersion

component.^{4–7} This problem of DFT has been extensively discussed in the literature—see Ref. 4 for a review and a quantitative analysis.

The most time-consuming terms in the currently programmed set of SAPT expressions⁸ are those describing the influence of electron correlation *within* monomers on interaction energies. If these terms are neglected, the resulting method, denoted by SAPT(0), becomes computationally orders of magnitude faster, but the accuracy of the interaction potentials produced by SAPT(0) is inadequate for many purposes. Williams and Chabalowski⁹ have proposed a perturbational approach in which the interaction energies are obtained from the SAPT(0) expressions with the Hartree-Fock (HF) orbitals and eigenvalues replaced by the Kohn-Sham (KS) ones. We will refer to this approach as SAPT(KS). Unfortunately, the accuracy of the SAPT(KS) predictions was found to be not better than that of SAPT(0). This was true for all components of interaction energy, including the electrostatic energy. In the latter case, the poor results were particularly disappointing since the electrostatic energy is

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potentially exact in the SAPT(KS) approach. Williams and Chabalowski⁹ conjectured that the poor accuracy of the SAPT(KS) electrostatic energies could be due to the known wrong behavior of DFT densities at large distances from atoms or molecules. In a subsequent development, two of us¹⁰ and, independently, Hesselmann and Jansen¹¹ have confirmed this conjecture by applying an asymptotic correction to the exchange-correlation potential which resulted in very accurate electrostatic energies. Also the exchange and induction energies were found to be remarkably accurate.^{10–12}

Very recently, the investigations of Ref. 10, performed for the helium and water dimers, were extended to the neon and carbon dioxide dimers and to include more functionals and larger basis sets.¹³ In some cases, significant discrepancies between SAPT and (asymptotically corrected) SAPT(KS) predictions have been initially observed. In most cases, the discrepancies were found to be related to the basis-set convergence. For some of the investigated dimers, the earlier SAPT calculations—which provided reference data for SAPT(KS)—used fairly small basis sets. When the SAPT results were recomputed with much larger bases and extrapolated to the complete basis-set (CBS) limit, the agreement with SAPT(KS) results—well-converged already in small bases—improved significantly. This finding is a confirmation of the soundness of the SAPT(KS) method. If the B97 class^{14–17} or PBE0 (Ref. 18) functionals are used (with asymptotic corrections) for the helium, neon, and water dimers, the discrepancies between the SAPT(KS) results for the sum of the electrostatic, induction, and exchange components and the reference SAPT results obtained using very large basis sets and the highest currently available level of intramonomer correlation were between 0.2% and 5%. This is a very satisfactory agreement taking into account that the corresponding errors for SAPT(0) are 8%–33%. For the carbon dioxide dimer, the analogous errors of SAPT(KS) were 7%–21%, whereas SAPT(0) gives a result of the wrong sign. Using the SAPT(KS) approach, one can compute the discussed components significantly faster than with the conventional SAPT approach including the intramonomer correlation effects. In fact, the time of calculations of these components becomes completely negligible compared to the time needed for DFT calculations on monomers and integral transformations.

For the neon and water dimers, it was possible to compute¹³ the reference values for the electrostatic energy at a higher level of theory than in the standard SAPT program,⁸ namely, at the coupled cluster with singles and doubles (CCSD) level, and to estimate the contribution from triple excitations. The SAPT(KS) energies agreed better with these more accurate benchmarks than with the standard electrostatic energies.⁸ For the carbon dioxide dimer, the same was found by estimating the exact electrostatic energy using asymptotic information. Thus, although the SAPT values of the electrostatic interaction energy are treated as benchmarks, one cannot exclude that the SAPT(KS) results can be more accurate in some cases, and the same may be true for other components.

Reference 13 provided a theoretical justification of the good performance of SAPT(KS) for the electrostatic and the

first-order exchange energy. The leading term of the second-order induction energy can be calculated with or without response effects.¹⁹ If this term is expressed via the static density susceptibilities,^{19,20} the two approaches correspond to the use of uncoupled or coupled susceptibilities, respectively. Jansen and Hesselmann²¹ pointed out that only the coupled Kohn-Sham (CKS) susceptibilities can give potentially exact induction energy, whereas the SAPT(KS) induction energy⁹ corresponds to the use of the uncoupled ones. It is interesting that the SAPT(KS) calculations^{9,10} led to very accurate induction energies despite using the uncoupled theory. The results obtained later in the coupled approach^{12,13} were, in fact, on average not more accurate than the uncoupled ones. The good performance of the uncoupled approach results apparently from a fortuitous but systematic cancellation of errors in the polarizabilities with errors in the charge penetration contribution to the induction energy.¹³ The expected lesser accuracy of the uncoupled approximation does, however, show up at large intermonomer separations.

The SAPT(KS) approach has been successful for the electrostatic, induction, and exchange components. For the dispersion energy, which represents the main intermolecular correlation effect, the errors are too large to enable computations of quantitatively correct interaction potentials. A solution to this problem was presented by three of us²² and independently by Hesselmann and Jansen.²³ This solution utilizes the frequency-dependent density susceptibilities computed using the time-dependent coupled Kohn-Sham (TD-CKS) theory in a dispersion energy expression generalizing the well-known Casimir-Polder formula to finite intermonomer distances. This generalization, taking into account the mutual penetration of molecular charge densities (i.e., the charge-overlap effects), was formulated by McLachlan²⁴ (in a relativistic form) and by Longuet-Higgins²⁵ (in the nonrelativistic limit) and was later rediscovered by Zaremba and Kohn,²⁶ by Dmitriev and Peinel,²⁷ and by McWeeny.²⁸ The method of computing the dispersion energy proposed in Refs. 22 and 23 turned out to be remarkably accurate. For the helium, neon, and water dimers considered in Ref. 22, the dispersion energies at equilibria were recovered to within 3%. In the present paper, after a short review of regular SAPT in Sec. II, we will provide a complete presentation of this new method of computing dispersion energies (Sec. III) and report (Sec. VI) numerical calculations for a range of intermonomer separations for the three systems considered in Ref. 22 and also for the carbon dioxide dimer (the latter results are presented as an EPAPS supplement²⁹). The complete interaction energies for these systems will be obtained using the so-called SAPT(DFT) approach described in Sec. V. By definition, this approach utilizes the electrostatic and first-order exchange energies from SAPT(KS), the induction and dispersion energies from CKS theory, and scaled SAPT(KS) expressions for the exchange-induction and the exchange-dispersion energies. The SAPT(DFT) approach has recently been applied to the argon, krypton, and benzene dimers,³⁰ providing excellent agreement with the best available potentials for these systems. We shall also describe the approximate procedures to compute the CKS dispersion energy which can be applied to study the interactions of large

polyatomic molecules. Specifically, we shall consider a density-fitting technique (Secs. IV and VII) and simplified schemes to compute the kernel in the CKS equations (Sec. VIII).

II. PERTURBATION THEORY OF INTERMOLECULAR INTERACTIONS

The interaction energy in SAPT is usually represented as a double perturbation expansion

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

where indices i and j denote the orders with respect to the intermolecular interaction operator V and the sum $W = W_A + W_B$ of intramonomer Møller-Plesset perturbation operators, respectively. For precise definition of $E_{\text{pol}}^{(ij)}$ and $E_{\text{exch}}^{(ij)}$ and for a discussion of the convergence behavior of the SAPT series, see Refs. 1, 2, 31, and 32. Up to the second order in V , the SAPT expansion can also be written as

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

where the summation over j has been carried out and the superscript refers now to the perturbation order in V : $E_{\text{pol}}^{(i)} = \sum_{j=0}^{\infty} E_{\text{pol}}^{(ij)}$ and $E_{\text{exch}}^{(i)} = \sum_{j=0}^{\infty} E_{\text{exch}}^{(ij)}$. The SAPT(0) level of theory is obtained by neglecting the intramonomer correlation operator W , i.e., taking only the corrections $E_{\text{pol}}^{(i0)}$ and $E_{\text{exch}}^{(i0)}$, $i=1$ and 2. The cumulative effect of the operator W , up to the k th order, is defined by

$$\epsilon_{\text{elst}}^{(n)}(k) \equiv \sum_{l=1}^k E_{\text{elst}}^{(nl)}, \quad (3)$$

for the electrostatic energy and similarly for other components appearing in Eq. (2). The interaction energy computed using the SAPT2002 suite of codes⁸ is the sum of the following corrections:

$$\begin{aligned} E_{\text{int}}^{\text{SAPT}} = & E_{\text{elst}}^{(10)} + \epsilon_{\text{elst,resp}}^{(1)}(3) + E_{\text{exch}}^{(10)} + \epsilon_{\text{exch}}^{(1)}(\text{CCSD}) \\ & + E_{\text{ind,resp}}^{(20)} + {}^tE_{\text{ind}}^{(22)} + E_{\text{exch-ind,resp}}^{(20)} + {}^tE_{\text{exch-ind}}^{(22)} \\ & + E_{\text{disp}}^{(20)} + \epsilon_{\text{disp}}^{(2)}(2) + E_{\text{exch-disp}}^{(20)}, \end{aligned} \quad (4)$$

see Refs. 1, 2, 19, and 33–36 for detailed definitions of the individual terms. The component $\epsilon_{\text{disp}}^{(2)}(2)$ is the most expensive part of a SAPT calculation since the time needed to compute it scales as $n_o^3 n_v^4$ with the number of occupied (n_o) and virtual (n_v) orbitals of the monomer (for a homogeneous dimer case). It is also possible to approximate $E_{\text{disp}}^{(2)}$ by performing a selective summation of certain classes of terms (diagrams) up to infinite order in W .^{37–40} For many systems, the effects of the third and higher orders in V are fairly important, especially for small internuclear separations. In conventional SAPT calculations, these effects are usually accounted for by the inclusion of the correction term

$$\delta E_{\text{int,resp}}^{\text{HF}} = E_{\text{int}}^{\text{HF}} - E_{\text{elst}}^{(10)} - E_{\text{exch}}^{(10)} - E_{\text{ind,resp}}^{(20)} - E_{\text{exch-ind,resp}}^{(20)}, \quad (5)$$

where $E_{\text{int}}^{\text{HF}}$ is the supermolecular interaction energy computed at the Hartree-Fock level (with the counterpoise correction).^{41,42}

III. DISPERSION ENERGY IN TERMS OF DENSITY SUSCEPTIBILITIES

The second-order dispersion energy, including the short-range, penetration (or charge-overlap) contribution, is defined by the formula

$$E_{\text{disp}}^{(2)} = \sum_{k \neq 0} \sum_{l \neq 0} \frac{|\langle \Phi_0^A \Phi_0^B | V \Phi_k^A \Phi_l^B \rangle|^2}{E_0^A + E_0^B - E_k^A - E_l^B}, \quad (6)$$

where Φ_i^X and E_i^X are the exact wave functions and energies for the i th state of monomer X . This quantity can be expressed through monomer's frequency-dependent density susceptibilities (FDDSs)

$$\begin{aligned} \alpha_X(\mathbf{r}, \mathbf{r}' | \omega) = & 2 \sum_{k \neq 0} \frac{(E_k^X - E_0^X)}{(E_k^X - E_0^X)^2 - \omega^2} \langle \Phi_0^X | \hat{\rho}_X(\mathbf{r}) | \Phi_k^X \rangle \\ & \times \langle \Phi_k^X | \hat{\rho}_X(\mathbf{r}') | \Phi_0^X \rangle, \end{aligned} \quad (7)$$

where $\hat{\rho}_X(\mathbf{r})$ is the electronic density operator, $\hat{\rho}_X(\mathbf{r}) \equiv \sum_{i \in X} \delta(\mathbf{r} - \mathbf{r}_i)$. The expression for the dispersion energy in terms of FDDSs reads^{25–28}

$$\begin{aligned} E_{\text{disp}}^{(2)} = & -\frac{1}{2\pi} \int_0^\infty \int \int \int \int \alpha_A(\mathbf{r}_1, \mathbf{r}'_1 | i\omega) \\ & \times \alpha_B(\mathbf{r}_2, \mathbf{r}'_2 | i\omega) \frac{d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{d\mathbf{r}'_1 d\mathbf{r}'_2}{|\mathbf{r}'_1 - \mathbf{r}'_2|} du. \end{aligned} \quad (8)$$

The uncoupled (UC) approximation to FDDSs is obtained if the exact functions and energies in Eq. (7) are replaced by their HF/KS counterparts [we will use indices $a(b)/r(s)$ to denote occupied/virtual orbitals of monomer $A(B)$]

$$\alpha_A^{\text{UC}}(\mathbf{r}, \mathbf{r}' | \omega) = 4 \sum_{ar} \frac{(e_r - e_a)}{(e_r - e_a)^2 - \omega^2} \phi_a(\mathbf{r}) \phi_r(\mathbf{r}) \phi_a(\mathbf{r}') \phi_r(\mathbf{r}'), \quad (9)$$

where e_i are orbital energies and ϕ_i are HF or KS orbitals, which are always assumed to be real. The dispersion energy in the uncoupled HF (UCHF) or uncoupled KS (UCKS) approximation, given by

$$E_{\text{disp}}^{(2)}(\text{UC}) = 4 \sum_{ar} \sum_{bs} \frac{(v_{ab}^{rs})^2}{e_a + e_b - e_r - e_s}, \quad (10)$$

where $v_{ab}^{rs} = \langle \phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) | r_{12}^{-1} | \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) \rangle$, is identical to the dispersion energy $E_{\text{disp}}^{(20)}$ of the conventional SAPT (Ref. 33) or to the approximation appearing in the SAPT(KS) theory,¹³ respectively.

The time-dependent CHF (TD-CHF) theory or TD-CKS theory in the adiabatic approximation^{43,44} gives the following expression for FDDSs:

$$\alpha_A(\mathbf{r}, \mathbf{r}' | \omega) = \sum_{ar, a'r'} C_{ar, a'r'}(\omega) \phi_a(\mathbf{r}) \phi_r(\mathbf{r}) \phi_{a'}(\mathbf{r}') \phi_{r'}(\mathbf{r}'), \quad (11)$$

with the coefficients $C_{ar, a'r'}(\omega)$ given by

$$C_{ar, a'r'}(\omega) = 4[(\mathbf{H}^{(2)}\mathbf{H}^{(1)} - \omega^2\mathbf{I})^{-1}\mathbf{H}^{(2)}]_{ar, a'r'}, \quad (12)$$

where \mathbf{I} is the unit matrix and, in the CKS theory, the Hessian matrices are defined as⁴⁵

$$\begin{aligned} \mathbf{H}_{ar, a'r'}^{(1)} &= (e_r - e_a) \delta_{aa'} \delta_{rr'} + 4v_{ra}^{ar'} \\ &+ 4 \int \phi_a \phi_r \phi_{a'} \phi_{r'} \frac{\delta v_{xc}}{\delta \rho} d\mathbf{r} \end{aligned} \quad (13)$$

and $\mathbf{H}_{ar, a'r'}^{(2)} = (e_r - e_a) \delta_{aa'} \delta_{rr'}$. In the CHF theory, the last term of Eq. (13) (involving the exchange-correlation potential v_{xc}) is absent and the matrices $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(2)}$ acquire the contributions $-(v_{a'r'}^{ar'} + v_{ra}^{a'r'})$ and $-(v_{a'r'}^{ar'} - v_{ra}^{a'r'})$, respectively, resulting from the Hartree-Fock exchange. The current-density term considered in Ref. 44 has not been included here in the definition of $\mathbf{H}^{(2)}$ of the CKS theory as this term is computationally expensive and has been found to have a negligible effect on relevant molecular properties such as the dynamic polarizability and C_6 dispersion coefficient.⁴⁵

Equation (11) shows that the density susceptibilities can be easily extracted from programs calculating dynamic polarizabilities or other response functions. In our work, the CADPAC code⁴⁶ was used. The functional derivative of the exchange-correlation potential v_{xc} that appears in Eq. (13) is evaluated for each of the DFT functionals applied in this work using Eqs. (10) and (11) from Ref. 47 that have been programed in the CADPAC code.⁴⁶ For hybrid functionals which involve a fraction ξ of the HF exchange, the matrices $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(2)}$ acquire the HF exchange contributions $-\xi(v_{a'r'}^{ar'} + v_{ra}^{a'r'})$ and $-\xi(v_{a'r'}^{ar'} - v_{ra}^{a'r'})$, respectively, and the kernel $\delta v_{xc}/\delta \rho$ is replaced by its hybrid counterpart $\delta(v_{xc} - \xi v_x)/\delta \rho$, where v_x is the exchange part of v_{xc} [of a local-density approximation (LDA) or generalized-gradient approximation (GGA) type]. If FDDs expressed via Eq. (11) are substituted in Eq. (8), one obtains the following expression for the dispersion energy:

$$\begin{aligned} E_{\text{disp}}^{(2)} &= -\frac{1}{2\pi} \sum_{ar} \sum_{bs} \sum_{a'r'} \sum_{b's'} v_{ab}^{rs} v_{a'b'}^{r's'} \\ &\times \int_0^\infty C_{ar, a'r'}(iu) C_{bs, b's'}(iu) du, \end{aligned} \quad (14)$$

IV. DENSITY FITTING

The number of operations needed to evaluate Eq. (14) scales as $n_o^3 n_v^3$. Although this scaling is rather high, the prefactor is relatively small and the evaluation of the integral in Eq. (13) containing the functional derivative of v_{xc} takes much more time for systems of practical interest. However, if a monomer-centered basis-set (MCBS) is used, the CKS calculations can be performed once per potential-energy surface and then the evaluation of Eq. (14) will dominate the com-

putation time. It has been noticed in Ref. 22 that the calculations of formula (14) can be sped up by orders of magnitude if the products of orbitals that are functions of the same coordinates such as $\phi_a(\mathbf{r})\phi_r(\mathbf{r})$ are replaced by expansions in terms of an auxiliary one-electron basis $\sum_k D_{ar, k} \chi_k^A(\mathbf{r})$. One can then write $E_{\text{disp}}^{(2)}$ as

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_0^\infty \text{Tr}[\tilde{\mathbf{C}}^A(iu) \mathbf{J}(\tilde{\mathbf{C}}^B)^T(iu) \mathbf{J}^T] du, \quad (15)$$

where \mathbf{X}^T is the transposition of matrix \mathbf{X} , Tr denotes the trace of a matrix, and the matrix elements are

$$J_{kk'} = \iint \frac{\chi_k^A(\mathbf{r}) \chi_{k'}^B(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (16)$$

and

$$\tilde{C}_{kl}^A(\omega) = \sum_{ar, a'r'} D_{ar, k} C_{ar, a'r'}(\omega) D_{a'r', l}. \quad (17)$$

The fitting coefficients $D_{ar, k}$ are obtained using the weighted least-squares method

$$D_{ar, k} = \sum_l (\mathcal{S}^{-1})_{kl} \mathcal{T}_{ar, l}, \quad (18)$$

with $\mathcal{T}_{ar, l} = \iint \phi_a(\mathbf{r}_1) \phi_r(\mathbf{r}_1) w(\mathbf{r}_1, \mathbf{r}_2) \chi_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$ and $\mathcal{S}_{kl} = \iint \chi_k(\mathbf{r}_1) w(\mathbf{r}_1, \mathbf{r}_2) \chi_l(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$. As the weight function we have chosen $|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ (for all types of auxiliary basis sets). This choice results in a robust fit in the sense^{48,49} that the error in the integral $\iint \rho_{ar}(\mathbf{r}) \rho_{bs}(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d\mathbf{r} d\mathbf{r}'$ is of second order with respect to the errors in the transition densities. The property of the “robustness” holds strictly only when each of the transition densities is fitted with the same auxiliary basis set, i.e., if auxiliary functions $\chi_k^A(\mathbf{r})$ form a dimer-centered basis set. The two- and three-index Coulomb integrals \mathcal{S}_{kl} and $\mathcal{T}_{ar, k}$ were obtained from the four-index Coulomb integrals produced by CADPAC and GAMESS(US) (Ref. 50) by using the standard four-center integrals with one or two-orbitals replaced by s functions with the exponent 10^{-10} . It should be stressed that the density-fitting procedure described above was designed to speed up the evaluation of Eq. (14) and not the computation of the density susceptibility functions themselves. The latter has recently been achieved in the context of SAPT(DFT) in Refs. 51 and 52.

The scaling of the computational cost of the successive steps in the calculation of the dispersion energy are as follows (assuming homogeneous dimers).

- Calculation of Hessians: The monomer integral transformations and the computation of the v_{xc} -dependent part of the Hessian determine the costs and scale as $n_o n^4$, where $n = n_o + n_v$, and $n_o^2 n_v^2 n_a$, where n_a is the number of atoms, respectively. The latter step involves, however, a very large prefactor and dominates calculations for systems considered here (see also Sec. VIII).
- Calculation of $C_{ar, a'r'}(\omega)$: The multiplication and inversion of matrices of order $n_o n_v$ need to be repeated for I frequencies ω : $n_o^3 n_v^3 I$, but the prefactor of this step is small. I is typically between 8 and 16.

- Evaluation of $D_{ar,k}$: The construction of the S_{kl} and $\mathcal{T}_{ar,k}$ matrices scales as m^2 and $n_o n_v^2 m$, respectively, the calculation of the inverse matrix $(S^{-1})_{kl}$ scales as m^3 , and the matrix multiplication in Eq. (18) that scales as $n_o n_v m^2$.
- Calculation of the transformed coefficients $\tilde{C}_{kl}^X(\omega)$: The transformation can be performed in two steps which scale as $n_o^2 n_v^2 m$ and $n_o n_v m^2$.
- Calculation of the J_{kl} integrals: m^2 .
- Calculation of $E_{\text{disp}}^{(2)}$ through Eq. (15): $m^3 I$.

If MCBS is used, the first four steps do not depend on the dimer geometry and have to be performed *only once* in the calculations for thousands of grid points needed to obtain a potential-energy surface. The remaining two steps need to be repeated for each point, but are very inexpensive. The slow MCBS convergence (see Sec. VI B) can be improved by surrounding each monomer by a “layer” of functions playing the role of the midbond functions in the monomer-centered “plus” basis sets (MC+BS).⁵³ Preliminary tests⁵⁴ show that this approach is quite promising.

V. THE SAPT(DFT) METHOD

In this section, we specify how the interaction energy of the SAPT(DFT) method proposed by us is defined. The corrections $E_{\text{elst}}^{(1)}$ and $E_{\text{exch}}^{(1)}$ are obtained within the SAPT(KS) approach,¹³ i.e., by using KS orbitals in the expressions for $E_{\text{elst}}^{(10)}$ and $E_{\text{exch}}^{(10)}$, respectively. The computational cost of obtaining $E_{\text{elst}}^{(1)}$ and $E_{\text{exch}}^{(1)}$ scales as n_o^2 and n_o^4 , respectively, and is negligible compared to the cost of the integral transformation (for simplicity, we assume homogeneous dimers in the discussions of scalings).

The second-order induction energy, $E_{\text{ind}}^{(2)} = E_{\text{ind}}^{(2)}(A) + E_{\text{ind}}^{(2)}(B)$, can be expressed via FDDSs evaluated at zero frequency.²⁰ In terms of the $C_{ar,a'r'}(\omega)$ coefficients of Eq. (11), which can be computed in the (U)CKS or (U)CHF approximations, $E_{\text{ind}}^{(2)}(A)$ can be written as

$$E_{\text{ind}}^{(2)}(A) = -\frac{1}{2} \sum_{aa'rr'} C_{ar,a'r'}(0)(\omega_B)_{ar}(\omega_B)_{a'r'}, \quad (19)$$

where $(\omega_B)_{ar}$ are the matrix elements of the electrostatic potential of molecule B . When Eq. (19) is evaluated with the $C_{ar,a'r'}(0)$ coefficients of the UCKS theory, one obtains the induction energy of SAPT(KS), denoted by $E_{\text{ind}}^{(2)}(\text{UCKS})$. The induction energy included in SAPT(DFT), denoted by $E_{\text{ind}}^{(2)}(\text{CKS})$, is defined by Eq. (19) with the $C_{ar,a'r'}(0)$ coefficients obtained from the CKS equations. Details of our implementation are described in Ref. 13. The expression of Eq. (19) is algorithmically very simple and its evaluation cost scales as only $n_o^2 n_v^2$, provided the coefficients $C_{ar,a'r'}(0)$ are known. When the basis set used in a calculation includes functions on the partner monomer site,⁵³ which is necessary to obtain saturated values of $E_{\text{ind}}^{(2)}(\text{CKS})$, the coefficients $C_{ar,a'r'}(0)$ must be recalculated for every dimer geometry. It may be noted that it is possible to compute the sum of the induction and exchange-induction energies using a regular-

ized Coulomb potential.³² In this case MCBS can be used and the monomer CKS coefficients can be computed only once per surface.

Since the exchange-induction energy cannot be expressed in terms of response functions and electron densities of monomers, we estimate this quantity by scaling the SAPT(KS) result $E_{\text{exch-ind}}^{(2)}(\text{KS})$,

$$\tilde{E}_{\text{exch-ind}}^{(2)}(\text{CKS}) = E_{\text{exch-ind}}^{(2)}(\text{KS}) \frac{E_{\text{ind}}^{(2)}(\text{CKS})}{E_{\text{ind}}^{(2)}(\text{UCKS})}. \quad (20)$$

We use the tilde sign to denote the approximate nature of the above expression. The cost of computing $E_{\text{exch-ind}}^{(2)}(\text{KS})$ scales as $n_v n_o^4$.

The expression for the second-order dispersion energy in terms of the FDDS's has been described in Sec. III. The exchange-dispersion energy is estimated by scaling the SAPT(KS) result $E_{\text{exch-disp}}^{(2)}(\text{KS})$, similarly as for the exchange-induction energy

$$\tilde{E}_{\text{exch-disp}}^{(2)}(\text{CKS}) = E_{\text{exch-disp}}^{(2)}(\text{KS}) \frac{E_{\text{disp}}^{(2)}(\text{CKS})}{E_{\text{disp}}^{(2)}(\text{UCKS})}. \quad (21)$$

The cost of calculating $E_{\text{exch-disp}}^{(2)}(\text{KS})$ scales as $n_o^3 n_v^2$.

The total interaction energy in the SAPT(DFT) method through second order in the intermonomer interaction operator V is defined as

$$\begin{aligned} E_{\text{int}}^{\text{SAPT(DFT)}} &= E_{\text{elst}}^{(1)}(\text{KS}) + E_{\text{exch}}^{(1)}(\text{KS}) + E_{\text{ind}}^{(2)}(\text{CKS}) \\ &\quad + \tilde{E}_{\text{exch-ind}}^{(2)}(\text{CKS}) + E_{\text{disp}}^{(2)}(\text{CKS}) \\ &\quad + \tilde{E}_{\text{exch-disp}}^{(2)}(\text{CKS}). \end{aligned} \quad (22)$$

When the effects beyond second order in V are expected to be important, these effects can be included by adding the $\delta E_{\text{int,resp}}^{\text{HF}}$ correction discussed in Sec. II. The necessity of calculating the terms in Eq. (5) does not change the algorithmic scaling of the SAPT(DFT) method.

VI. NUMERICAL RESULTS

To better assess the effectiveness SAPT(DFT), we shall present comparisons involving not only the total values of individual terms in Eq. (22) but also the hard-to-compute “intramonomer correlation” part of a given interaction energy component. For conventional SAPT, this intramonomer correlation contribution is defined by Eq. (3). For SAPT(DFT), the intramonomer correlation part of $E^{(n)}(\text{CKS})$ is defined as

$$\epsilon^{(n)}(\text{CKS}) = E^{(n)}(\text{CKS}) - E^{(n0)}, \quad (23)$$

where $E^{(n)}(\text{CKS})$ stands for a SAPT(DFT) interaction energy component and the reference “uncorrelated” values $E^{(n0)}$ are defined in the SAPT(0) approximation (based on the Hartree-Fock orbitals), see Sec. II. For the induction and exchange-induction components, the reference SAPT(0) energies include the response effects, i.e., we use the CHF quantities $E_{\text{ind,resp}}^{(20)}$ and $E_{\text{exch-ind,resp}}^{(20)}$ instead of $E_{\text{ind}}^{(20)}$ and $E_{\text{exch-ind}}^{(20)}$. All terms in Eq. (23) were always computed using the same basis set. Similar definition $\epsilon^{(n)}(\text{KS}) = E^{(n)}(\text{KS}) - E^{(n0)}$ is used for the SAPT(KS) quantities.

The accuracy of the interaction energy components: $E_{\text{elst}}^{(1)}(\text{KS})$, $E_{\text{exch}}^{(1)}(\text{KS})$, $E_{\text{ind}}^{(2)}(\text{KS})$, $E_{\text{ind}}^{(2)}(\text{CKS})$, and $E_{\text{exch-ind}}^{(2)}(\text{KS})$ was discussed in detail in Ref. 13. Here we will consider only their sum

$$\Sigma(\text{CKS}) = E_{\text{elst}}^{(1)}(\text{KS}) + E_{\text{exch}}^{(1)}(\text{KS}) + E_{\text{ind}}^{(2)}(\text{CKS}) + \tilde{E}_{\text{exch-ind}}^{(2)}(\text{CKS}) \quad (24)$$

and a similar sum involving the SAPT(KS) induction and exchange-induction energies

$$\Sigma(\text{KS}) = E_{\text{elst}}^{(1)}(\text{KS}) + E_{\text{exch}}^{(1)}(\text{KS}) + E_{\text{ind}}^{(2)}(\text{KS}) + E_{\text{exch-ind}}^{(2)}(\text{KS}). \quad (25)$$

The sum of the analogous components from Eq. (4) will be denoted as $\Sigma(\text{SAPT})$. The interaction energy components included in Eqs. (24) and (25) are sensitive to physics of the short-range, intramonomer electron correlation, but do not involve the effects of the long-range correlation of the motion of electrons belonging to different monomers. The latter effects are responsible for the dispersion and exchange-dispersion contributions, sensitive to both the inter- and intramonomer correlations, and therefore much more difficult to compute accurately.

The isotropic, or spherically averaged, C_6 dispersion coefficient provides a convenient way of assessing the accuracy of the methods used to compute the second-order dispersion energy, particularly when accurate benchmark results are not available at finite intermolecular separations. This quantity is defined as

$$C_6 = \frac{3}{\pi} \int_0^\infty \bar{\alpha}^A(iu) \bar{\alpha}^B(iu) du, \quad (26)$$

where $\bar{\alpha}^X(\omega) = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ is the isotropic dynamic dipole polarizability of monomer X . $E_{\text{disp}}^{(2)}$ behaves asymptotically as $C_6(2)/R^6$, where the constant $C_6(2)$ can be calculated from zeroth-, first-, and second-order many-body perturbation theory (MBPT) approximations to dynamic polarizabilities⁵⁵ using the POLCOR (Ref. 56) program. The C_6 constant of the CKS theory has been obtained using the CADPAC (Ref. 46) codes.

A. Density functionals

The HCTH407,⁵⁷ PBE0,¹⁸ and B97-2 (Ref. 17) exchange-correlation functionals have been used in this work. These are among the best representatives of the continuum and hybrid exchange-correlation functionals currently available. Of these, PBE0 is of special significance as it is the hybrid counterpart of the PBE (Ref. 58) functional which has been constructed to satisfy many physical constraints without fitting to experimental data. In contrast, HCTH407 and B97-2 are fitted to reproduce a large body of both *ab initio* and experimental data.

It has been demonstrated in Refs. 10 and 13 that the asymptotic correction must be applied to the exchange-correlation potentials resulting from the above functionals if the van der Waals interaction energy components are to be recovered accurately. The Fermi-Amaldi (FA) (Ref. 59) long-range form together with the splicing scheme of Tozer and

Handy (TH) (Ref. 47) have been used to implement the asymptotic correction; the details are given in Ref. 13. The effectiveness of asymptotic correction in SAPT(DFT) has already been well documented in the literature,^{10-13,22} therefore only corrected results will be presented here. For simplicity, we will not explicitly indicate the use of this correction. As in Ref. 13, to remove any ambiguity that might arise if the ionization potentials needed for the asymptotic correction are obtained theoretically, we have chosen to use the experimental values from Ref. 60.

B. Convergence with basis set

It has been shown in Ref. 13 that the energy components present in Eq. (24) (i.e., not sensitive to the long-range correlation) saturate much faster with basis-set size in the case of the SAPT(KS) than the regular SAPT approach. This behavior is related to the well-known difficulties that the orbital basis sets encounter in describing the interelectronic cusps in many-electron wave functions. No such cusps appear in SAPT(KS) at the Σ level. The same is not true for the dispersion energy in either UCKS or CKS approach. As the UCKS/CKS dispersion energy expressions are formally equivalent to those of the UCHF/CHF method, we expect a similar basis-set sensitivity in both approaches. The basis-set convergence in the latter case is well known. The dispersion energy converges slowly in the MCBS format, in particular, when the standard, intramonomer correlation-optimized functions are used.⁵³ The convergence can be improved by optimizing the basis sets' exponents to minimize the dispersion energy. However, the most significant improvement is achieved by adding a small number of functions located at the midpoint between the interacting monomers. This leads to the MC+BS form of the basis sets.⁵³ Such sets usually contain also a small number of functions centered on the interacting partner. If all functions from the partner's basis are included, the dimer-centered plus basis-set (DC+BS) format results. The functions on the interacting partner further improve the dispersion energy, but to a much lesser degree than the functions located on the bond. The strategy for most of the SAPT calculations from our group was to use the MC+BS approach with dispersion-optimized exponents for medium accuracy calculations. The bases denoted by the letter A below are examples taken from past calculations. Despite their small size, these bases provide quite accurate (to within a few percent) values of $E_{\text{disp}}^{(20)}$. If a higher accuracy of the interaction energy is needed, it is not sufficient to further improve the saturation of the $E_{\text{disp}}^{(20)}$ component since the errors resulting from a poor representation of intramonomer correlation components become more significant. To improve these components, one has to add functions with exponents optimized for the monomer correlation energies. The important finding of Ref. 13 was that the bases of type A appear to saturate well the short-range, intramonomer correlation effects in the DFT-based approach. Thus, such bases or larger ones, with more dispersion-optimized exponents should provide well-converged results in SAPT(DFT). This hypothesis will be tested below.

In Table I, we report the $E_{\text{disp}}^{(2)}(\text{CKS})$ values for the he-

TABLE I. The basis-set convergence of $E_{\text{disp}}^{(2)}$ (CKS). Results are reported for internuclear separations of 5.6 bohrs for He_2 and 3.1 Å for Ne_2 . All calculations are with the asymptotically corrected PBE0 functional. Cartesian functions have been used for all basis sets. Units are kelvins for He_2 and cm^{-1} for Ne_2 .

Basis	Basis sets	Refs.	Basis format		
	atom/midbond/farbond		MCBS	MC+BS	DC+BS
Helium dimer					
Dc71	[7s3p2d1f]/[3s2p1d]/[7s]	64 and 53	-21.25	-22.45	-22.62
Dc147	[7s5p4d3f]/[3s2p1d1f]/[7s]	64 and 64	-21.44	-22.87	-22.94
Neon dimer					
A	[5s3p2d1f]/[3s2p1d1f]/[5s3p]	61 and 64	-49.46	-57.95	-58.17
aVTZ	[5s4p3d2f]/[3s2p1d1f]/[5s4p]	62 and 64	-41.29	-58.67	-58.92
aVQZ' ^a	[6s5p4d3f]/[3s2p1d1f]/[6s5p]	62 and 64	-46.85	-59.32	-59.55
daVTZ	[6s5p4d3f]/[3s2p1d1f]/[6s5p]	63 and 64	-50.49	-59.60	-59.88
daVQZ' ^a	[7s6p5d4f]/[3s2p1d1f]/[7s6p]	63 and 64	-52.42	-59.76	-60.01

^aThe prime denotes the removal of functions of g symmetry.

lium and neon dimers obtained using different basis sets. The near-minimum configurations with internuclear separations of 5.6 bohrs and 3.1 Å have been used for He_2 and Ne_2 , respectively. All basis sets contain Cartesian Gaussian functions. For each type of the monomer basis, calculations of $E_{\text{disp}}^{(2)}$ (CKS) have been performed with three formats of the full basis set: (1) MCBS, (2) MC+BS (including also the isotropic functions of the monomer's partner), and (3) DC+BS. The specific compositions of the basis sets and references are given in Table I. The Dc71 and Dc147 basis sets used for He_2 have polarization functions optimized for both the intra- and intermonomer correlations. For the neon dimer, we have used a relatively small basis developed in Ref. 61 and denoted as Basis(A) in Ref. 13, as well as four types of correlation-consistent basis sets:⁶² the aug-cc-pVTZ (aVTZ), aug-cc-pVQZ with g functions removed (aVQZ'), daug-cc-pVTZ (daVTZ), and daug-cc-pVQZ with g functions removed (daVQZ'). The removal of g functions was necessary as CADPAC does not allow higher functions than f . The 3s2p1d1f set of midbond functions was included in MC+BS and DC+BS formats. The use of midbond functions will be indicated by the notation like in aVQZ'+Mb.

From Table I, the following observations can be made.

- For both He_2 and Ne_2 , the $E_{\text{disp}}^{(2)}$ (CKS) energy computed using the largest basis sets in DC+BS format is well converged with respect to basis-set extension. For He_2 , we may expect that the residual error is less than 1% since the same basis set gives -17.07 K for $E_{\text{disp}}^{(20)}$, i.e., a 0.6% error compared to the exact result of -17.17 K (Ref. 64). For Ne_2 , we do not know the exact result but the convergence pattern suggests that the largest DC+BS gives the dispersion energy accurate to within a few tenths of cm^{-1} . This is confirmed by the X^{-3} extrapolations from the aug and d-aug sequences that give -60.0 and -60.1 cm^{-1} , respectively.
- When the MC+BS format is used, the loss of accuracy compared to the DC+BS results is almost negligible, as it is in the conventional SAPT calculations.⁵³

- With the MCBS format, the $E_{\text{disp}}^{(2)}$ (CKS) energies obtained using various basis sets differ from the near converged value by about 7% for He_2 (ratio computed with respect to -22.94 K) and by 13%–31% for Ne_2 (ratio computed with respect to -60.0 cm^{-1}). This illustrates the slow convergence in the MCBS format (but keep in mind that MCBS sizes are much smaller than the corresponding DCBS ones) and also shows that the atom-centered parts of the helium basis sets are relatively more complete than their neon counterparts. Basis(A), containing only 39 functions in the Cartesian MCBS format, gives somewhat better results than the aVTZ and aVQZ' bases, showing the importance of using the dispersion-optimized exponents in the MCBS format. As shown in Ref. 53, to achieve the convergence in the MCBS format, one has to use high angular momentum orbitals. This has not been possible at the moment due to the restrictions of CADPAC. Very recently, we were able to perform a calculation of the CKS dispersion energy of helium dimer using a newly developed interface to the DALTON package.⁶⁵ With the LDA functional, the spherical [7s5p4d3f2g1h1i] basis of Ref. 53 in the MCBS format (105 functions) recovered 97.6% of the value computed using spherical daV6Z+3s3p2d2f1g basis in the DC+BS format (372 functions). The Dc71 basis in DC+BS format recovers also about 98% of the dispersion energy. Thus, despite the need for high angular functions, the sizes of MCBS basis sets do not need to be much larger than those of DC+BS basis sets of comparable accuracy. The performance of MCBS-type basis sets is important for the efficiency of the density-fitting approach.

These observations are similar to those made in Ref. 53 regarding the convergence of $E_{\text{disp}}^{(20)}$. We also see that the small dispersion-optimized basis sets that were found to perform very well when applied to the KS/CKS Σ -level corrections¹³ are adequate for the calculations of dispersion energies as well.

TABLE II. The interaction energy components for He_2 at $R=5.6$ a.u. obtained from SAPT and SAPT(DFT). All energies in kelvins. The benchmark results include intramonomer correlation effects up to infinite order, while SAPT results up to the second order, i.e., the highest order available in the SAPT2002 program (Ref. 8). The Cartesian Dc147 basis was used in DC⁺BS form both in SAPT and SAPT(DFT) calculations. The term $\Delta^{(3-\infty)}$, containing contributions of the third and higher order in V , is taken from Ref. 64.

Comp.	Benchmark (Ref. 64)	SAPT	SAPT(DFT) ^a		
			HCTH407	B97-2	PBE0
$\Sigma(\text{SAPT})$ or $\Sigma(\text{CKS})$	10.54	10.57 ^b	11.00	10.63	10.94
$\Sigma(\text{KS})$			11.00	10.63	10.94
$E_{\text{disp}}^{(20)}$	-17.17	-17.07			
$\epsilon_{\text{disp}}^{(2)}$ or $\epsilon_{\text{disp}}^{(2)}(\text{CKS})$	-5.23	-4.29 ^c	-5.98	-5.55	-5.87
$\epsilon_{\text{disp}}^{(2)}(\text{UCKS})$			-8.72	-5.98	-6.29
$E_{\text{exch-disp}}^{(20)}$	0.54	0.51			
$\epsilon_{\text{exch-disp}}^{(2)}$ or $\epsilon_{\text{exch-disp}}^{(2)}(\text{CKS})$	0.20	...	0.19 ^d	0.17 ^d	0.19 ^d
$\epsilon_{\text{exch-disp}}^{(2)}(\text{UCKS})$			0.27	0.18	0.20
$E_{\text{int}} = E^{(1)} + E^{(2)}$	-11.12	-10.28	-11.36 ^c	-11.31 ^c	-11.31 ^c
$E_{\text{int}} + \Delta^{(3-\infty)}$	-11.06	-10.22	-11.30	-11.26	-11.25

^aThe $E^{(n0)}$ energies subtracted from SAPT(DFT) correlation energies are those listed in SAPT column.

^bSAPT(0) gives $\Sigma=9.65$ K (with relaxed components, wherever possible).

^c $\epsilon_{\text{disp}}^{(2)}(2)$.

^dObtained using Eq. (21).

^eComputed as in Eq. (22).

C. Accuracy of the second-order dispersion and exchange-dispersion energies

1. Helium dimer

The availability of accurate benchmarks⁶⁴ for the helium dimer makes it an important system for testing purposes. Calculations for both SAPT and SAPT(DFT) were performed using the Dc147/DC⁺BS basis described already in Sec. VI B. An ionization potential of 0.9036 a.u. (Ref. 60) was used in the calculations. The “benchmark” interaction energy components are taken from Table V in Korona *et al.*⁶⁴ who consider these to be the best estimates of each component. These values were computed using either Gaussian geminals, a basis Mc191,⁶⁴ or the Dc147 basis and are basis-set converged to approximately 0.01 K.

In Table II, the interaction energy components for the near-minimum internuclear separation of 5.6 bohrs from SAPT and SAPT(DFT) are listed together with the benchmark values. The quantity $\epsilon_{\text{disp}}^{(2)}$, i.e., the intra-atomic correlation contribution to $E_{\text{disp}}^{(2)}$, obtained from CKS is in error of 6%–14% for the different functionals used. This can be contrasted with the error of 18% made by conventional SAPT at the currently programmed theory level. For the total dispersion energy, the corresponding errors are 1%–3% and 5%, respectively. In Fig. 1(a), the correlation contribution $\epsilon_{\text{disp}}^{(2)}$ from the SAPT, CKS, and UCKS approaches is plotted together with the benchmark values for a range of internuclear separations. The agreement for all three functionals with the benchmark is remarkable for all internuclear separations. In particular, CKS with B97-2 is almost equal to the benchmark. By comparison, $\epsilon_{\text{disp}}^{(2)}$ from conventional SAPT is systematically too positive for all distances. Since SAPT values are expected to be nearly basis set converged, this discrepancy must originate from contributions to the dispersion energy arising from intramonomer correlation effects of the third and higher orders in the operator W . The UCKS values of

$\epsilon_{\text{disp}}^{(2)}$ are also close to the benchmark for the B97-2 and PBE0 functionals. This apparently good performance is probably accidental, as He_2 is the only system for which such agreement has been found.

Also reported in Table II is the quantity $\epsilon_{\text{exch-disp}}^{(2)}$. SAPT(DFT) is seen to recover the benchmark value with errors of 5%–15%, similar to those for the dispersion energy. At present, there is no other system for which the values of

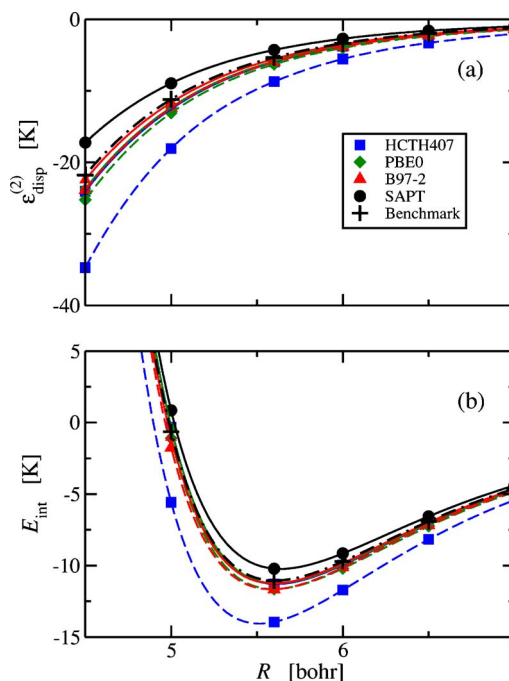


FIG. 1. Intra-atomic correlation contribution to the dispersion interaction (upper panel) and total interaction energy [with $\Delta^{(3-\infty)}$] for helium dimer. The Cartesian Dc147 basis was used in the DC⁺BS form. The CKS values are represented by the solid lines, while the dashed lines correspond to UCKS. Squares: HCTH407; diamonds: PBE0; triangles-up: B97-2; closed-circles: SAPT; plus signs: benchmark results from Ref. 64.

TABLE III. The isotropic C_6 dispersion coefficient for the four dimers studied in this work. The MBPT2 values are asymptotically equivalent to $E_{\text{disp}}^{(2)}(2)$ from SAPT and are computed using the POLCOR (Ref. 56) program. CKS calculations have been performed with CADPAC (Ref. 46). The calculations with POLCOR have utilized basis sets with spherical Gaussians, while calculations with CADPAC have utilized Cartesian Gaussian orbitals. All values are reported in atomic units.

System	SAPT (MBPT2)	CKS			Benchmark
		HCTH407	B97-2	PBE0	
He ₂	1.400 ^a	1.489 ^a	1.472 ^a	1.488 ^a	1.461 ^b
Ne ₂	6.316 ^c	6.248 ^d	6.159 ^d	6.234 ^d	6.383 ^c
(H ₂ O) ₂	47.23 ^f	45.32 ^f	45.04 ^f	45.25 ^f	45.37 ^g
(CO ₂) ₂	191.6 ^h	148.9 ^h	147.8 ^h	148.3 ^h	158.7 ⁱ

^aMonomer part of Dc147 basis.

^bReference 66.

^caug-cc-pV5Z basis.

^daug-cc-pVQZ' (no *g* functions) basis.

^eReference 67.

^faug-cc-pVTZ basis.

^gReference 68.

^hMonomer part of Basis(A).

ⁱReference 69.

$\epsilon_{\text{exch-disp}}^{(2)}$ are known (this correction has not yet been developed in the general-purpose SAPT program) so it is not possible to say if the accuracy exhibited by SAPT(DFT) for He₂ holds more generally.

The C_6 coefficients for He₂ obtained using the CKS dynamic polarizabilities are shown in the first row of in Table III and compared with the best literature value and with the coefficient $C_6(2)$ determining the asymptotics of $E_{\text{disp}}^{(2)}(2)$. The C_6 values obtained with the three DFT functionals differ from the benchmark by 1%–2%, while $C_6(2)$ is 4% lower than the benchmark. This provides further evidence of the accuracy that can be attained with the CKS, and hence SAPT(DFT), methodology.

2. Neon dimer

The basis aVQZ' + 3s2p1d1f described in Sec. VI B was used in SAPT(DFT) calculations for Ne₂ in the Cartesian MC+BS format. SAPT(KS) interaction energy components in this basis have been found to be sufficiently converged¹³ (see also Table I). An ionization potential of 0.7925 a.u. (Ref. 60) was used to perform the asymptotic correction. For SAPT, we used the basis set mentioned above and also the larger aug-cc-pV5Z basis⁶² in the MC+BS format with the same midbond functions and utilizing spherical orbitals. SAPT interaction energy components computed in this basis set were found¹³ to be converged to 0.01–0.5 cm^{−1}. Unlike the case for the helium dimer, near-exact benchmark results do not exist for the neon dimer. Thus, basis-set-converged SAPT results have to suffice as a reference against which SAPT(DFT) is to be tested. However, one should realize that SAPT interaction energy components are susceptible to errors arising from inadequacies in the level of theory used to account for intramonomer correlation, see Ref. 13.

In Table IV, the conventional SAPT and SAPT(DFT) interaction energy components are reported for a near-minimum intermonomer separation of $R=3.1$ Å. The intra-atomic correlation contribution $\epsilon_{\text{disp}}^{(2)}$ from SAPT(DFT) differs from the SAPT/CBS value by 3%–18%, depending on the functional used. From Table III, we see that the C_6 coefficient from SAPT agrees with the benchmark value to 1%, while those from SAPT(DFT) have somewhat larger differ-

ences of 2%–3.5%. This suggests that, for this dimer, $E_{\text{disp}}^{(2)}(2)$ from SAPT is slightly more accurate than that from SAPT(DFT). However, the differences are small enough to be accounted for by basis-set incompleteness effects. In Fig. 2(a), $\epsilon_{\text{disp}}^{(2)}$ values are plotted for different internuclear separations. The excellent agreement of SAPT and SAPT(DFT) is evident. In contrast to the helium dimer, $\epsilon_{\text{disp}}^{(2)}$ from UCKS calculations is very poor, yielding values that are consistently too negative. The correlation contribution $\tilde{\epsilon}_{\text{exch-disp}}^{(2)}$ from SAPT(DFT) is around 1 cm^{−1}, and is thus non-negligible.

3. Water dimer

We fixed the relative orientation of the water molecules at their minimum geometry⁷⁰ (monomers in their vibrationally averaged geometry, dimer in C_s symmetry, nonlinearity of hydrogen bond of 8.5°, and the angle of the acceptor bisector with the vector joining centers of mass of 129.3°) and calculated the interaction energy for various center-of-mass separations. The basis set used for SAPT(DFT) and SAPT calculations was taken from Ref. 70 and consisted of [5s3p2d1f] functions on O, [5s3p] on H, and [3s2p1d] on the mid-bond. This basis will be denoted as Basis(A) and was used with Cartesian Gaussian functions in DC+BS format. It was demonstrated in Ref. 13 that SAPT interaction energy components in Basis(A) are not completely converged. Using SAPT calculations in two larger basis sets, the CBS limit for SAPT was estimated. Due to computational costs of the SAPT calculation in large basis sets, this estimate was performed at two separations ($R=2.6$ and 3 Å). An ionization potential of 0.4638 a.u. (Ref. 60) was used to perform the asymptotic correction.

As with the neon dimer, the basis-set-converged SAPT results have to serve as the reference against which SAPT(DFT) will be compared. Table V shows that the component $\epsilon_{\text{disp}}^{(2)}$ from SAPT(DFT) differs from the SAPT/CBS results by 3%–9%. At the same time, $\epsilon_{\text{disp}}^{(2)}$ from SAPT with Basis(A) differs from SAPT/CBS by 27%, of course, due exclusively to the deficiencies of Basis(A). Table III shows that the isotropic C_6 dispersion coefficient at the theory level corresponding to SAPT is 4% too large while those corresponding to SAPT(DFT) (i.e., the CKS coefficients) are 0.1%–0.7%

TABLE IV. Comparison of the interaction energy components for Ne₂ from SAPT in aug-cc-pV5Z + [3s2p1d1f] spherical MC⁺BC and from SAPT and SAPT(DFT) in aug-cc-pVQZ' + [3s2p1d1f] Cartesian MC⁺BS. Internuclear separation is 3.1 Å. All energies are in cm⁻¹.

Component	SAPT			SAPT(DFT) ^a		
	aVQZ'	aV5Z+Mb	CBS ^b	HCTH407	B97-2	PBE0
Σ (SAPT) or Σ (CKS)	29.09 ^c	28.58 ^d	28.43 ^c	28.95	27.40	28.50
Σ (KS)				28.95	27.39	28.48
$E_{\text{disp}}^{(20)}$	-46.20	-46.46	-46.69			
$\epsilon_{\text{disp}}^{(2)}$ or $\epsilon_{\text{disp}}^{(2)}$ (CKS)	-12.12 ^f	-11.87 ^g	-11.74 ^f	-13.82	-12.08	-13.13
$\epsilon_{\text{disp}}^{(2)}$ (UCKS)				-26.81	-19.02	-20.19
$E_{\text{exch-disp}}^{(20)}$	1.86	1.86	1.87			
$\tilde{\epsilon}_{\text{exch-disp}}^{(2)}$ (CKS)				1.09 ^g	0.91 ^g	1.02 ^g
$\tilde{\epsilon}_{\text{exch-disp}}^{(2)}$ (UCKS)				1.72	1.23	1.35
$E_{\text{int}} = E^{(1)} + E^{(2)}$	-27.36	-27.88	-28.13	-28.12 ^h	-28.10 ^h	-27.94 ^h
$E_{\text{int}} + \delta E_{\text{int,resp}}^{\text{HF}}$	-27.90	-28.51	-28.77	-28.66 ⁱ	-28.64 ⁱ	-28.49 ⁱ
$E_{\text{int}}[\text{CCSD}(T)]$		-28.40				

^aThe $E^{(n0)}$ energies subtracted from SAPT(DFT) correlation energies are those from SAPT in Cartesian aug-cc-pVQZ' + [3s2p1d1f] basis.

^bFrom Ref. 13.

^cSAPT(0) gives $\Sigma = 20.36$ cm⁻¹ (with relaxed components, wherever applicable).

^dSAPT(0) gives $\Sigma = 20.42$ cm⁻¹ (with relaxed components, wherever applicable).

^eSAPT(0) gives $\Sigma = 20.56$ cm⁻¹ (with relaxed components, wherever applicable).

^f $\epsilon_{\text{disp}}^{(2)}$.

^gObtained using Eq. (21).

^hComputed as in Eq. (22).

ⁱ $\delta E_{\text{int,resp}}^{\text{HF}}$ is the same as in SAPT/aVQZ' + Mb.

too small compared with the benchmark value. Notice that since upon basis-set extension all the C_6 coefficients will become larger, the SAPT/CBS C_6 will be somewhat less accurate whereas the CKS ones may compare even better with the benchmark.

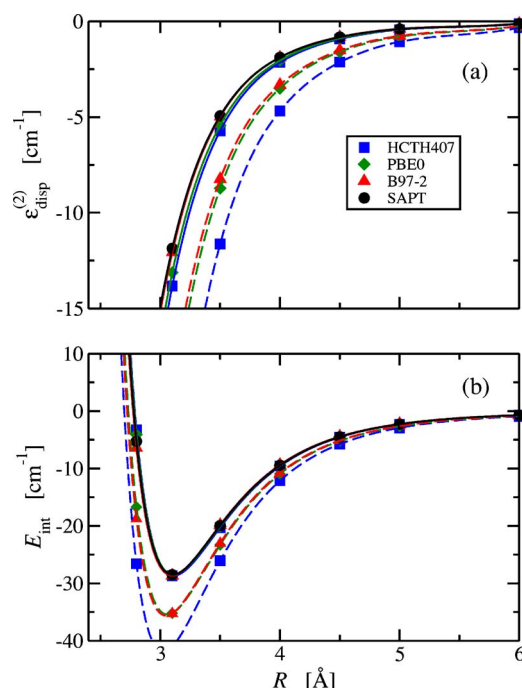


FIG. 2. Intra-atomic correlation contribution to the dispersion interaction (upper panel) and total interaction energy (with $\delta E_{\text{int,resp}}^{\text{HF}}$) for neon dimer. The Cartesian aug-cc-pVQZ' + [3s2p1d1f] basis was used in the MC⁺BS form for SAPT(DFT). The SAPT results are in spherical aug-cc-pV5Z + [3s2p1d1f]/MC⁺BS. Legend description as in Fig. 1.

The intramonomer correlation contribution $\tilde{\epsilon}_{\text{exch-disp}}^{(2)}$ from SAPT(DFT) is very small (0.05 kcal/mol) at this geometry, and is probably not important for this system.

In Fig. 3(a), values of $\epsilon_{\text{disp}}^{(2)}$ are plotted for SAPT, CKS, and UCKS—all in Basis(A). The SAPT and CKS curves differ substantially at small intermonomer separations. [The turnover in $\epsilon_{\text{disp}}^{(2)}$, exhibited by all three CKS curves, is also visible in SAPT results at smaller distances, not shown in the figure]. As at the minimum distance, it is mainly the basis-set deficiency that makes the SAPT/Basis(A) results to differ so much from CKS values. The SAPT/CBS values, shown at $R = 2.6$ and 3.0 Å, are very close to the CKS results.

D. Accuracy of the total interaction energy

1. Helium dimer

Before discussing the total interaction energies, let us briefly discuss the “dispersionless” energies Σ , sensitive only to the short-range correlation. From Table II, we can see that this quantity is reproduced by SAPT(DFT) with different functionals with errors of 1%–4%, whereas SAPT gives an error of 0.3%. Σ (CKS) and Σ (KS) agree to all digits listed Table II. The two sets of values are also extremely close for all other dimers investigated here. The main reason for this closeness is that the CKS and UCKS values of the induction energies are very similar, as discussed in Ref. 13. Furthermore, the CKS exchange-induction correction is computed by scaling the UCKS one. Since the induction and exchange-induction energies cancel to a large extent in the region of van der Waals minimum, this procedure tends to diminish the differences between the KS and CKS values of Σ .

If the dispersion and exchange-dispersion energies are added to Σ (CKS), the resulting sum of the first and second

TABLE V. Interaction energy components for the water dimer at $R=3$ Å. Basis(A) was used in Cartesian DC+BS form. CBS results for SAPT have been obtained in Ref. 13. All energies are in kcal/mol.

Component	SAPT Basis(A)	SAPT ^a CBS	SAPT(DFT): Basis(A) ^a		
			HCTH407	B97-2	PBE0
$\Sigma(\text{SAPT})$ or $\Sigma(\text{CKS})$	-2.03 ^b	-2.38	-2.17	-2.40	-2.38
$\Sigma(\text{KS})$			-2.25	-2.39	-2.35
$E_{\text{disp}}^{(20)}$	-2.10	-2.15			
$\epsilon_{\text{disp}}^{(2)}$ or $\epsilon_{\text{disp}}^{(2)}(\text{CKS})$	-0.42 ^c	-0.33 ^c	-0.32	-0.30	-0.30
$\epsilon_{\text{disp}}^{(2)}(\text{UCKS})$			-1.32	-0.90	-0.90
$E_{\text{exch-disp}}^{(20)}$	0.35	0.36	0.35	0.35	0.35
$\epsilon_{\text{exch-disp}}^{(2)}(\text{CKS})$			0.06 ^d	0.05 ^d	0.06 ^d
$\epsilon_{\text{exch-disp}}^{(2)}(\text{UCKS})$			0.22	0.15	0.16
$E_{\text{int}} = E^{(1)} + E^{(2)}$	-4.20	-4.50	-4.18 ^c	-4.40 ^c	-4.37 ^c
$E_{\text{int}} + \delta E_{\text{int,resp}}^{\text{HF}}$	-4.88	-5.18	-4.87 ^f	-5.08 ^f	-5.05 ^f
$E_{\text{int}}[\text{CCSD}(T)]$	-4.79				

^aThe $E^{(n0)}$ energies subtracted from SAPT(DFT) correlation energies are those from SAPT in Basis(A).

^bSAPT(0) gives $\Sigma = -3.16$ kcal/mol (with relaxed components, wherever possible).

^c $\epsilon_{\text{disp}}^{(2)}$.

^dObtained using Eq. (21).

^eComputed as in Eq. (22).

^f $\delta E_{\text{int,resp}}^{\text{HF}}$ is taken from SAPT in Basis(A).

orders (in V) energy components, E_{int} , is recovered by SAPT-(DFT) with an error of only 2%, whereas for SAPT the error is 8%. According to Ref. 64, the contributions from the third and higher orders in V , denoted by $\Delta^{(3-\infty)}$, is very small at the minimum, amounting only to 0.06 K compared to the total interaction energy of -11.06 K. Thus, for He_2 , the second-order treatment in V provides an excellent approximation and comparisons at this level are adequate.

In Fig. 1(b), the total interaction energies from SAPT, SAPT(DFT), SAPT(KS), and the benchmark calculation are

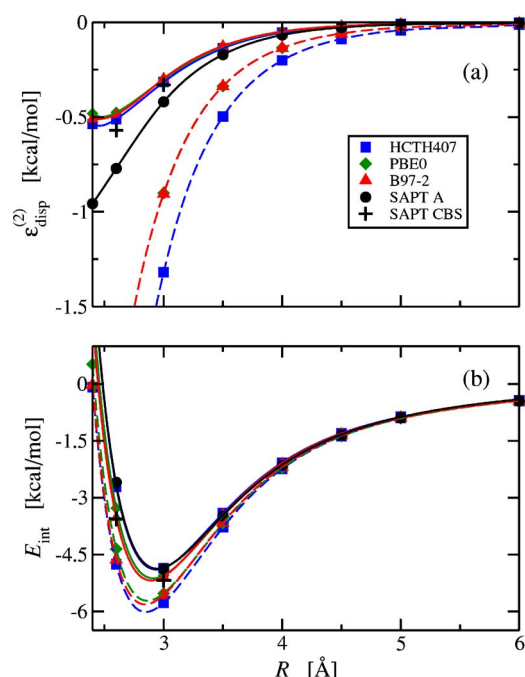


FIG. 3. Intramolecular correlation contribution to the dispersion interaction (upper panel) and total interaction energy (with $\delta E_{\text{int,resp}}^{\text{HF}}$) for water dimer. Angular configuration as described in the text. The Cartesian Basis(A) was used in DC+BS form. Legend description as in Fig. 1.

plotted for a range of internuclear separations. The observations made for $R=5.6$ bohrs are seen to hold for all separations. The agreement of all three SAPT(DFT) curves with the benchmark results is remarkable. The SAPT curve is consistently too high, while the SAPT(KS) curves are slightly too low (except for HCTH one which is significantly too low). It should be noted that Hesselmann and Jansen⁷¹ performed recently a very similar calculation for the helium dimer using the exact exchange-correlation potential (available for two-electron systems), rather than the GGA approximations used by us, and also obtained excellent agreement with benchmark results. Overall, the performance of SAPT(DFT) for He_2 is outstanding. It extends over the whole range of interatomic separations and does not result from cancellations of errors since the individual components are accurate as well.

2. Neon dimer

Table IV shows that the values of $\Sigma(\text{CKS})$ and $\Sigma(\text{SAPT})/\text{CBS}$ differ by 0.2%–4%. The total interaction energies from SAPT and SAPT(DFT) are in extremely close agreement, with differences of only 0.2%–0.9%, clearly partly due to cancellation of errors between the components. For comparison, we computed the interaction energy at the CCSD(T) level in the aV5Z+Mb basis set. SAPT and SAPT-(DFT) interaction energies are in good agreement with the CCSD(T) result, differences being only 1.3% for SAPT/CBS, 0.4% for SAPT in the same basis, and between 0.3% and 0.9% for SAPT(DFT). The $\delta E_{\text{int,resp}}^{\text{HF}}$ correction generally improves the agreement of SAPT/SAPT(DFT) results with the CCSD(T) interaction energy (although not by much). This is probably fortuitous since this correction should not be used for interactions of nonpolar systems, as discussed earlier. The excellent agreement between SAPT and SAPT(DFT) energies is reflected in Fig. 2(b) where the total interaction energy is plotted for a range of intermonomer separations. The curves are almost on top of each other, the

TABLE VI. The second-order dispersion energy computed using the density-fitting technique of Sec. IV. Calculations have been performed at the near-minimum separations specified earlier. All calculations are with the asymptotically corrected PBE0 functional. Units are kelvins for the helium dimer and cm^{-1} for the neon dimer. Main basis sets are Cartesian aug-cc-pVXZ limited to up to f functions in MCBS form. Auxiliary basis sets for density fitting are taken from Ref. 72.

Basis/size	Energy	Helium dimer	
		Auxiliary basis/size	Density-fitted energy
aQZ[5s4p3d2f]/55	-19.72	aux-aQZ'[6s5p4d3f]/75	-19.52
a5Z'[6s5p4d3f]/75	-20.42	aux-a5Z'[7s6p5d4f]/95	-20.24
Neon dimer			
aVQZ'[6s5p4f3f]/75	-46.85	aux-aVQZ'[9s8p7d6f4g]/195	-46.90
aV5Z'[7s6p5d4f]/95	-50.82	aux-aV5Z'[11s9p8d7f5g]/231	-50.76

discrepancies are visible only for the smallest R . Also plotted in Fig. 2 are the SAPT(KS) values of the total interaction energy, significantly too negative.

3. Water dimer

From Table V, we first see that the two hybrid functionals recover the CBS extrapolated value of $\Sigma(\text{SAPT})$ virtually exactly. At the same time, $\Sigma(\text{SAPT})$ obtained with Basis(A) differs by 15% from the corresponding CBS value. The total interaction energy from SAPT(DFT) up to second order in V differs from the SAPT/CBS value by 2%–7%, while SAPT in Basis(A) differs from the same value by about 7%. The CCSD(T) interaction energy in Basis(A) agrees to within 0.1 kcal/mol with E_{int} from SAPT in the same basis, showing the fast convergence in the level of theory for the water dimer.

In Fig. 3(b), the total interaction energy (with $\delta_{\text{int,resp}}^{\text{HF}}$) from the SAPT, SAPT(DFT), and SAPT(KS) methods is plotted for various separations. We can see that whereas the HCTH407 results agree closely but certainly accidentally with the SAPT/Basis(A) energies, B97-2 and PBE0 results are in very good agreement with the SAPT/CBS results.

VII. DENSITY-FITTING RESULTS

As discussed in Sec. IV, the density-fitting technique developed here leads to large savings in the computer time only if monomer-centered basis sets are used, therefore, in this section we restrict our attention to such bases. The MCBS format requires high angular momentum orbitals to obtain well-converged dispersion energies. Using such orbitals was not possible due to the restrictions of the CADPAC code. Thus, the dispersion energies presented in this section are not of high accuracy. Nevertheless, our results are sufficient to demonstrate the efficiency of the procedure.

Results of the calculations of $E_{\text{disp}}^{(2)}$ (CKS) with [using Eq. (15)] and without [using Eq. (14)] density fitting are presented in Table VI. Basis sets aQZ and a5Z' have been used for He_2 and aVQZ' and aV5Z' for Ne_2 , with primes again indicating the removal of orbitals of symmetries higher than f . The corresponding auxiliary basis sets⁷² are specified in Table VI. In the density-fitting codes, we were able to use orbitals of symmetries higher than f and such orbitals were

utilized if present in the auxiliary bases. Notice that one has to use the auxiliary basis fitted to a given original basis to achieve high accuracy results.

The results listed in Table VI show that the density fitting works very well. Although the auxiliary basis sets are at the most only about 2.5 times larger than the original ones, the accuracy of the density fitting is very high. For He_2 , the errors are about 1%, and for Ne_2 about 0.1%. The higher accuracy in the latter case is clearly connected with the larger auxiliary basis sets that are available for this system. However, already the former accuracy is completely satisfying as it will be rare that the original energies will be that accurate.

VIII. TYPE OF KERNEL

The bulk of the computational time in a CKS calculation is spent in evaluating the integral over the kernel $\delta v_{\text{xc}}/\delta \rho$ (and the product of four orbitals) in the definition of $\mathbf{H}^{(1)}$, cf. Eq. (13). For v_{xc} 's involving gradients of the density, this evaluation is computationally so demanding that for a wide range of systems it dominates complete SAPT(DFT) calculations. A dramatic simplification of this term occurs when the LDA functional is used. For the four systems studied in this work, the LDA $\mathbf{H}^{(1)}$ Hessian is evaluated up to ten times faster compared to the case of a gradient-corrected v_{xc} . Moreover, with LDA approximations, the techniques of density fitting can be straightforwardly utilized in evaluation of $\mathbf{H}^{(1)}$.^{43,73} Of course, the use of LDA for the whole DFT calculation would lead to results of low accuracy. However, it is possible to employ a gradient-corrected potential everywhere in the calculations except for the evaluation of the kernel which is performed using the LDA formula and the density produced by a given gradient-corrected v_{xc} . Note that this approach is often referred to as adiabatic LDA (ALDA) in calculations of molecular properties although this name is misleading since the adiabatic approximation is needed to get the CKS propagators with any kernel.

In Table VII, we present the results for $E_{\text{disp}}^{(2)}$ computed with $\mathbf{H}^{(1)}$ evaluated using the same v_{xc} as was in the KS calculations and the LDA approximation for the kernel $\delta v_{\text{xc}}/\delta \rho$. For hybrid functionals, the Hessians are evaluated with appropriate CHF exchange contributions and with the exchange part of the LDA kernel scaled by $(1-\xi)$. LDA works particularly well for the HCTH407 and PBE0 functionals, with errors smaller than 0.9%. The agreement is

TABLE VII. The second-order dispersion energy with the $\mathbf{H}^{(1)}$ Hessian evaluated using different approximations. Calculations have been performed at the near-minimum geometries utilized in the previous tables. The basis sets used are those described in the text. All of them were applied in the Cartesian DC*BS format, except for Ne_2 where MC*BS was used. He_2 : Dc147, Ne_2 : daVQZ', $(\text{H}_2\text{O})_2$: Basis(A), $(\text{CO}_2)_2$: Basis(A). Units used are kelvins, cm^{-1} , kcal/mol, and cm^{-1} for the helium, neon, water, and carbon dioxide dimers, respectively.

Functional/Hessian	He_2	Ne_2	$(\text{H}_2\text{O})_2$	$(\text{CO}_2)_2$
HCTH407/HCTH407	-23.05	-60.02	-2.42	-713.9
HCTH407/LDA	-22.95	-60.12	-2.41	-711.5
PBE0/PBE0	-22.94	-59.32	-2.40	-707.3
PBE0/LDA	-22.91	-59.31	-2.38	-700.9
B97-2/B97-2	-22.62	-58.27	-2.40	-702.3
B97-2/LDA	-22.26	-57.47	-2.33	-686.5

somewhat less satisfactory for B97-2/LDA where the differences are between 1.4% and 2.5%. Thus, the LDA approximation for the kernel will be particularly suitable for applications involving large molecules, where uncertainties related to the basis-set truncations will usually be larger than the errors due to this approximation.

IX. SUMMARY

We have demonstrated that the second-order dispersion energy can be computed to high accuracy using frequency-dependent density susceptibility functions from coupled Kohn-Sham theory. For the helium dimer, the only system for which accurate benchmarks are available, this method (with the B97-2 functional) is able to recover the near-exact dispersion energy to 1% at the minimum geometry. In contrast, the dispersion energy from conventional SAPT calculation is in error by 4.6%. For the neon and water dimers at the near-minimum geometries, the dispersion energy from the CKS/B97-2 method agrees with SAPT in the complete basis-set limit to 0.3% and 1.2%, respectively. For the carbon dioxide dimer, the dispersion energy from SAPT and the B97-2 functional differ by about 12% at the near-minimum dimer geometry.²⁹ Using an asymptotic analysis, we have shown that the CKS value is likely to be closer to the exact one. The conventional SAPT value is less accurate due to the lack of a sufficiently high level of intramonomer correlation in $E_{\text{disp}}^{(2)}$ (2).

When the electrostatic, first-order exchange, induction, and exchange-induction energies are combined with the dispersion and exchange-dispersion energies as described in Sec. V, the resulting theory—called SAPT(DFT)—is able to recover the total interaction energy for the helium, neon, water, and carbon dioxide dimers with an accuracy equal or possibly higher than that achieved by the currently programmed SAPT. For the helium dimer, SAPT(DFT) with B97-2 agrees with the very accurate benchmark interaction energy to 1.7% at the minimum with similar accuracies at all other internuclear separations, whereas SAPT at the currently programmed level differs from the benchmark by 7.6%. For the neon dimer, the conventional SAPT and SAPT(DFT) total interaction energies cannot be distinguished on a graph. For the water dimer, SAPT(DFT)/B97-2 agrees with the

complete basis-set limit of conventional SAPT to 1.9% at the near-minimum geometry. For the carbon dioxide dimer, SAPT(DFT) and CCSD(T) interaction energies agree to within 2.0%, while SAPT is more than 20% too deep compared to CCSD(T). We have shown that the basis-set convergence of SAPT(DFT) is better than that of the regular SAPT since the intramonomer correlation effects saturate quickly in SAPT(DFT) and therefore the basis sets can be optimized only from the point of view of dispersion interactions.

As discussed in Ref. 13, computational scaling of SAPT(KS) is much better than that of the conventional SAPT at the currently programmed theory level, the most demanding term scaling as $n_o^3 n_v^2$. The CKS dispersion energy scales as $n_o^3 n_v^3$, but this scaling can be reduced to only m^3 using density-fitting techniques. With modest auxiliary bases, the density-fitting technique yields dispersion energies that are about 1% off the values without fitting. The two-electron integral transformation that scales as $n_o(n_o + n_v)^4$ is required for the interaction energy components other than the dispersion energy and together with time-dependent DFT (TD-DFT) step dominate the time of calculation. However, very recently density-fitting techniques were implemented to speed up these steps considerably.^{52,74}

SAPT(DFT) is robust with respect to the choice of exchange-correlation functionals. While the hybrid functionals (PBE0 and B97-2) are clearly superior, the continuum functional HCTH407 also yields good interaction energies. We emphasize that in general all exchange-correlation potentials have to be asymptotically corrected to yield accurate interaction energies.^{10,13,22} Only for the CO_2 dimer, the application of the asymptotic correction does not seem to be necessary, but this conclusion should be checked with calculations in larger basis sets than used here.

The construction of the $\mathbf{H}^{(1)}$ Hessian needed for the calculation of the second-order energies is quite time consuming when gradient-corrected exchange correlation functionals are used. We have demonstrated that the Hessians can be constructed using the LDA approximation with a loss in accuracy of only up to 2.5%. This approximation results in calculations that are up to ten times faster compared with Hessians evaluated with gradient-corrected functionals. The LDA approximation, when combined with density-fitting techniques to evaluate the integrals appearing in $\mathbf{H}^{(1)}$,^{43,73} will result in an exceptionally efficient method of calculating interaction energies.

The computational efficiency and accuracy of SAPT(DFT) makes this method very suitable for investigations of interactions between large molecules. With current computational resources, calculations for dimers containing 40–60 atoms are feasible. We emphasize that our results for small systems indicate that SAPT(DFT) provides accuracy comparable with highly correlated methods such as CCSD(T)—at a fraction of the computational cost.

When this work was virtually completed, we obtained a preprint of a paper by Hesselmann *et al.*⁵¹ who also developed an efficient computer implementation of SAPT based on DFT theory. In particular, these authors developed and

implemented a very efficient density-fitting technique for computing density susceptibilities in dimer-centered basis sets.

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