REGULAR ARTICLE

Intermolecular exchange-induction energies without overlap expansion

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Abstract An approach to evaluate the second-order exchange-induction energies of symmetry-adapted intermolecular perturbation theory (SAPT) for single-determinant ground-state monomer wavefunctions has been derived. This approach is correct to all orders of the intermonomer overlap, that is, it takes multiple electron exchange between the monomers into account. The resulting formulae can be written in a compact way and implemented efficiently. Here, the method is employed to investigate the performance of the S^2- or single-exchange approximation at the Hartree-Fock-SAPT level. The list of test systems comprises the prototypical van der Waals- and hydrogen-bridge complexes Ne_2, Ar–HF, and $(H_2O)_2$, but also the systems HCl^-, $NeNa^+$ and Li^+F^- involving closed-shell ions. It was found that the errors introduced by the S^2-approximation are more pronounced for the second-order exchange-induction energy than for the first-order exchange energy. While these errors tend to be negligible throughout the well region of complexes such as the neon dimer, they start to be significant in the repulsive part of the well regions of systems such as the water dimer, and in particular for the ionic lithium fluoride molecule. The consequences of these findings for the Hartree-Fock level estimate of higher-order induction plus exchange-induction energies, which is frequently employed in SAPT are also discussed.

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1 Introduction

Symmetry-adapted perturbation theory (SAPT) has been developed as an alternative to supermolecular methods for the calculation of weak intermolecular interactions [1–3]. Up to second order in the interaction potential, this ansatz results in a splitting of the total interaction energy into first-order electrostatic and second-order induction and dispersion parts, accompanied by exchange corrections that arise from the antisymmetry of the total wavefunction:

$$E_{int} = E_{el}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{exch-ind}^{(2)} + E_{disp}^{(2)} + E_{exch-disp}^{(2)}.$$

(1)

Practical implementations of SAPT that account for the important intramonomer electron correlation effects on the interaction energy employing multi-determinant ground-state wavefunctions have first been made in the framework of many-body symmetry-adapted perturbation theory (MB-SAPT) [4–6].

In a multi-determinant approach, the calculation of the exchange corrections is somewhat involved due to the non-orthogonality of the orbitals of the respective monomers, a problem that in an approximation for the first-order exchange contribution was circumvented by Rijks, Gerritsen, and Wormer through a hole-particle orbital orthogonalization [7]. In the framework of SAPT, the so-called single-exchange or S^2-approximation was introduced early on [8–11]. It includes only terms up to the second order of

the intermonomer overlap. For single-determinant Hartree-Fock descriptions of the interacting monomers, it was shown that the resulting second-order exchange contributions can be written as Coulomb interactions between overlap intermolecular charge distributions [12]. To the best of our knowledge, no systematic study of the performance of the S^2-approximation for second-order exchange energies has been published so far, with the notable exception of a study of the helium dimer by Korona et al. [13] using correlated monomer wavefunctions. The calculations on the helium dimer, however, confirm the earlier suggestions that the S^2-approximation is an excellent approximation except for very small distances between the monomers. Thus, it is expected that in most cases, the quality of the well region of intermolecular potential energy surfaces is hardly diminished by the S^2-approximation, and this is the region of interest in most SAPT studies of non-covalently bound systems.

More recently a second possibility to account for intra-monomer electron correlation effects on the intermolecular interaction energy has been opened up through combining Kohn-Sham density functional theory (KS-DFT) with SAPT, leading to the DFT-SAPT [14–19] or, equivalently, SAPT(DFT) [20–26] methods. Within these approaches, the ground-state density of each monomer is obtained from a single-determinant wavefunction. As is well known, this wavefunction describes a pseudo-particle system—and not a true electronic system—chosen such that its density is exactly that of the corresponding electronic system. Similarly, the first-order correction to the ground-state wave-function of the pseudo-particle system delivered by solution of the static and frequency-dependent coupled-perturbed Kohn-Sham equations is only guaranteed to reproduce the linear change in the ground-state density of the true electronic system correctly. Therefore, the exchange contributions to SAPT interaction energies will not be exact in DFT-SAPT and SAPT(DFT) [14]. Nevertheless, a growing body of evidence shows that the replacement of the true electronic wavefunction and its perturbation wavefunctions with corresponding Kohn-Sham quantities is a good approximation in the framework of SAPT: in many cases, the resulting interaction energies rival the accuracy of the current gold standard in quantum chemistry, that is, single-and double-excitation-coupled cluster theory with perturbative triple excitations (CCSD(T)), as exemplified in Refs. [18, 27–30].

The first correction to the S^2-approximation of $E_{exch}^{(1)}$ containing terms of order S^4 has been derived and tested by van Duijneveldt-van de Rijt and van Duijneveldt for the case of a single-determinant Hartree-Fock (HF) description of the monomers [31]. Furthermore, an exact single-determinant expression for $E_{exch}^{(1)}$ containing all orders of S has been given by Jeziorski, Bulski, and Piela [32]. In

fact, this approach has regularly been employed in both MB-SAPT and DFT-SAPT. The determination of second-order interaction energy contributions requires singly and doubly excited determinants if the ground state of each monomer is a single determinant. Matrix elements involving the full Hamilton operator of the dimer and antisymmetrized products of monomer non-, singly-, and doubly-excited determinants have been derived and employed in an inter-molecular perturbation theory variant by Hayes and Stone [33, 34]. These matrix elements, which account for all orders of S, have been generalized to arbitrary excitation levels by Figari and Magnasco [35]. They are related to the matrix elements needed in a SAPT approach but do not exactly correspond to them: the latter exclusively involve the Coulomb interaction operators for all particles of one monomer with the particles of the other monomer.

In this paper, we will present an efficient approach to determine the second-order SAPT exchange-induction contribution $E_{exch-ind}^{(2)}$ without the S^2-approximation for single-determinant ground-state wavefunctions, taking electronic response into account at the coupled-perturbed Hartree-Fock (CPHF) level. With this, here, we will investigate the quality of the S^2-approximation of exchange–induction energies for six small, yet representative cases: (1) the Ne dimer as a prototype van der Waals complex, (2) the Ar–HF complex combining non-polar and polar monomers, (3) the water dimer as a prototype for hydrogen-bridged systems, (4) the complex HCl^- combining a compact rare-gas atom with a diffuse anion, (5) the system $NeNa^+$ which is isoelectronic to Ne_2, and (6) the LiF molecule as an example for a system with a strong ionic bond.

Besides potential applications in DFT-SAPT, the presented approach is also useful for determining the so-called δ(HF)-approximation for higher-order induction and exchange-induction contributions [36, 37] on a more accurate level. This approximation is defined as

$$\delta(\text{HF}) = E_{int}^{HF} - E_{el}^{(1)}(\text{HF}) - E_{exch}^{(1)}(\text{HF}) - E_{ind}^{(2)}(\text{HF}) \\ - E_{exch-ind}^{(2)}(\text{HF}), \tag{2}$$

where E_{int}^{HF} is the supermolecular interaction energy as calculated on the counter-poise-corrected (CP-corrected) [38] Hartree-Fock level and the other contributions on the r.h.s. are the standard SAPT interaction energy contributions as determined from the HF determinant (for the first-order contributions) and the linear CPHF wavefunction (for the second-order contributions), respectively. Note that the use of the δ(HF) contribution for the calculation of an improved SAPT interaction energy as

$$\tilde{E}_{int} = E_{int} + \delta(\text{HF}) \tag{3}$$

has been criticized on theoretical and pragmatic grounds: first one should note that E_{int}^{HF} as a supermolecular energy

contains contributions, which are absent in SAPT, and second, it was observed that while employing δ(HF) for hydrogen-bonded systems improves the interaction energies, it has an adverse effect on pure van der Waals systems such as rare-gas dimers [39, 40]. Here, we will not go into the second question but rather investigate the effect of the S^2-approximation on the behavior of δ(HF) with decreasing distance between the monomers. One should note that the addition of the δ(HF) to SAPT energies results in a hybrid method where essentially electron correlation effects on the interaction energy are added on top of a supermolecular HF interaction energy—an approach that may be preferable over non-hybrid SAPT for convergence reasons at small intermolecular distances where the mutual perturbation of the molecules is large. In this contribution, we will limit our attention to interaction energies without electron correlation contributions, that is, omitting $E_{disp}^{(2)}$ and $E_{exch-disp}^{(2)}$ from Eq. (1) and using HF and CPHF descriptions of the interacting monomers. We will denote the corresponding E_{int} as HF-SAPT interaction energies.

The outline of the paper is as follows: in the next section, an overview of the formalism will be given, followed by a section, collecting a brief discussion of some aspects, implementation and the computational details of our calculations. The results are presented and discussed next. Finally, some general conclusions and an outlook will be given.

2 Theory

In SAPT, the first-order interaction energy reads

$$E^{(1)} = E_{el}^{(1)} + E_{exch}^{(1)} = \frac{\langle \psi_0^A \psi_0^B | \hat{V} \hat{\mathcal{A}} | \psi_0^A \psi_0^B \rangle}{\langle \psi_0^A \psi_0^B | \hat{\mathcal{A}} | \psi_0^A \psi_0^B \rangle}, \quad (4)$$

where ψ_0^A and ψ_0^B are the ground-state wavefunctions of the isolated monomers A and B, respectively. The perturbation operator $\hat{V}$ collects the Coulomb interactions of all electrons and nuclei of monomer A with those of B, and $\hat{\mathcal{A}}$ denotes the antisymmetrizing operator for all $N = N_A + N_B$ electron indices. Approximating the exact ground-state wavefunctions with single normalized Slater determinants Φ_0^A and Φ_0^B composed of occupied spin-orbitals χ_i and χ_j, respectively, computation of the first-order energy requires the matrix elements $\langle \Phi_0^A \Phi_0^B | \hat{\mathcal{A}} | \Phi_0^A \Phi_0^B \rangle$ and $\langle \Phi_0^A \Phi_0^B | \hat{V} \hat{\mathcal{A}} | \Phi_0^A \Phi_0^B \rangle$. The evaluation of these matrix elements is known [32] and its results are only briefly repeated here to introduce our notation. Defining the overlap matrix $\mathbf{S}$ composed of the matrix elements

$$S_{rs} = \langle \chi_r | \chi_s \rangle, \quad (5)$$

where r and s label general occupied orbitals (irrespective on their location either on monomer A or B), one obtains

$$\langle \Phi_0^A \Phi_0^B | \hat{\mathcal{A}} | \Phi_0^A \Phi_0^B \rangle = \frac{N_A! N_B!}{N!} \det \mathbf{S} = \frac{N_A! N_B!}{N!} \mathcal{S}. \quad (6)$$

Defining

$$A_{jr} = \langle \chi_j | v_A | \chi_r \rangle, \quad (7)$$

$$B_{ir} = \langle \chi_i | v_B | \chi_r \rangle, \quad (8)$$

where v_A and v_B are the Coulomb potentials of the nuclei of monomers A and B, respectively, one further gets

$$\langle \Phi_0^A \Phi_0^B | \hat{V} \hat{\mathcal{A}} | \Phi_0^A \Phi_0^B \rangle$$
$$= \frac{N_A! N_B!}{N!} \left(W_{AB} \mathcal{S} + \sum_i \sum_r B_{ir} \mathcal{S}^{ir} + \sum_j \sum_r A_{jr} \mathcal{S}^{jr} \right.$$
$$\left. + \sum_i \sum_j \sum_r \sum_{s>r} \langle ij||rs \rangle \mathcal{S}^{ij,rs} \right), \quad (9)$$

where W_{AB} denotes the Coulomb interaction energy between the nuclei of monomers A and B and $\langle ij||rs \rangle$ an antisymmetrized two-electron integral in physicicsts' notation [41]. The symbol $\sum_i$ stands for summation over the occupied orbitals of monomer A, $\sum_j$ means summation over the occupied orbitals of monomer B, and $\sum_r$ and $\sum_s$ denote summation over all occupied orbitals. The second cofactors $\mathcal{S}^{ij,rs}$ are obtained by deleting rows i and j and columns r and s in $\det \mathbf{S}$ and multiplying the resulting subdeterminant with $(-1)^{i+j+r+s}$. Their definition is generalized to the cases $i > j$ and $r > s$ through requesting $\mathcal{S}^{ij,rs} = -\mathcal{S}^{ji,rs}$ and $\mathcal{S}^{ij,rs} = -\mathcal{S}^{ij,sr}$. They are related to first cofactors $\mathcal{S}^{ir}$ (obtained by deleting row number i and column r and multiplying the corresponding subdeterminant with $(-1)^{i+r}$) through a Jacobi identity [42]

$$\mathcal{S}^{ij,rs} = \frac{1}{\mathcal{S}} (\mathcal{S}^{ir} \mathcal{S}^{js} - \mathcal{S}^{is} \mathcal{S}^{jr}). \quad (10)$$

Noting that

$$\mathcal{S}^{ir} = \mathcal{S} D_{ri}, \quad (11)$$

where D_{ri} is an element of the inverse of the overlap matrix $\mathbf{D} = \mathbf{S}^{-1}$, the first-order energy becomes

$$E^{(1)} = W_{AB} + \sum_i \sum_r B_{ir} D_{ri} + \sum_j \sum_r A_{jr} D_{rj}$$
$$+ \frac{1}{2} \sum_i \sum_j \sum_r \sum_s \langle ij||rs \rangle (D_{ri} D_{sj} - D_{si} D_{rj}), \quad (12)$$

where further simplifications are possible due to the antisymmetry of $\langle ij||rs \rangle$. Subtracting the electrostatic contribution $E_{el}^{(1)}$ from Eq. (12) one explicitly obtains $E_{exch}^{(1)}$.

The second-order induction plus exchange-induction energy in SAPT reads

$$E_{\text{Ind}}^{(2)} = E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} = \frac{\langle \psi_0^A \psi_0^B | (\hat{V} - E^{(1)}) \hat{\mathcal{A}} | \Psi_{\text{ind}}^{(1)} \rangle}{\langle \psi_0^A \psi_0^B | \hat{\mathcal{A}} | \psi_0^A \psi_0^B \rangle}, \quad (13)$$

where the first-order induction wavefunction is given by

$$\Psi_{\text{ind}}^{(1)} = \Psi_{\text{ind,A}}^{(1)} + \Psi_{\text{ind,B}}^{(1)} = -(\hat{R}_0^A + \hat{R}_0^B)(\hat{V} - E^{(1)}) \psi_0^A \psi_0^B, \quad (14)$$

and $\hat{R}_0^A$ and $\hat{R}_0^B$ are the reduced ground-state resolvents of monomers A and B, respectively. In the framework of Hartree-Fock theory, the first-order induction wavefunction corresponding to polarization of monomer A is obtained from solving the coupled-perturbed Hartree-Fock equations as

$$\Psi_{\text{ind,A}}^{(1)} = \sum_i \sum_a C_{ia} \Phi_{i \to a}^A \Phi_0^B, \quad (15)$$

where $\Phi_{i \to a}^A$ denotes a singly excited Slater determinant with orbital χ_i replaced by a virtual orbital χ_a, and C_{ia} are the CPHF coefficients as obtained with the electric potential of monomer B as a perturbation. A similar equation holds for $\Psi_{\text{ind,B}}^{(1)}$. Thus, computation of the second-order induction energy requires matrix elements like $\langle \Phi_0^A \Phi_0^B | (\hat{V} - E^{(1)}) \hat{\mathcal{A}} | \Phi_{i \to a}^A \Phi_0^B \rangle$. Introducing the determinant $\mathcal{S}_{i \to a}$ that differs from $\mathcal{S}$ by replacing the elements S_{ri} in the ith column with $S_{ra} = \langle \chi_r | \chi_a \rangle$, some algebra involving expansion of determinants into first and second cofactors as

$$\mathcal{S}_{i \to a} = \sum_r S_{r \to a} \mathcal{S}^{ri},$$

$$\mathcal{S}_{i \to a}^{rs} = \frac{1}{\mathcal{S}} (\mathcal{S}_{i \to a} \mathcal{S}^{rs} - \mathcal{S}_{s \to a} \mathcal{S}^{ri}), \quad (16)$$

$$\mathcal{S}_{i \to a}^{rs,tu} = \frac{1}{\mathcal{S}} (\mathcal{S}_{i \to a} \mathcal{S}^{rs,tu} - \mathcal{S}_{t \to a} \mathcal{S}^{rs,iu} - \mathcal{S}_{u \to a} \mathcal{S}^{rs,ti})$$

leads to

$$\langle \Phi_0^A \Phi_0^B | (\hat{V} - E^{(1)}) \hat{\mathcal{A}} | \Phi_{i \to a}^A \Phi_0^B \rangle$$
$$= \frac{N_A! N_B!}{N!} \left(\sum_{i'} (B_{i'a} - \sum_r B_{i'r} \frac{\mathcal{S}_{r \to a}}{\mathcal{S}}) \mathcal{S}^{i'i} \right.$$
$$+ \sum_j (A_{ja} - \sum_r A_{jr} \frac{\mathcal{S}_{r \to a}}{\mathcal{S}}) \mathcal{S}^{ji}$$
$$\left. + \sum_{i'} \sum_j \sum_s (\langle i'j || as \rangle - \sum_r \langle i'j || rs \rangle \frac{\mathcal{S}_{r \to a}}{\mathcal{S}}) \mathcal{S}^{i'j,is} \right), \quad (17)$$

where A_{ja} and $B_{i'a}$ are the obvious generalizations of (7) and (8), respectively. Noting that

$$\mathcal{S}_{ia} = \mathcal{S} \sum_r D_{ir} S_{ra} = \mathcal{S} \sum_j D_{ij} S_{ja}, \quad (18)$$

where the last equation holds since a virtual orbital at monomer A can at most have an overlap with occupied

orbitals of B, making use of (10,11) and introducing the definitions

$$T_{ra} = \sum_j D_{rj} S_{ja}, \quad (19)$$

$$\tilde{B}_{i'a} = B_{i'a} - \sum_r B_{i'r} T_{ra}, \quad (20)$$

$$\tilde{A}_{ja} = A_{ja} - \sum_r A_{jr} T_{ra}, \quad (21)$$

$$\widetilde{\langle i'j || as \rangle} = \langle i'j || as \rangle - \sum_r \langle i'j || rs \rangle T_{ra} \quad (22)$$

we thus get

$$\frac{\langle \Phi_0^A \Phi_0^B | (\hat{V} - E^{(1)}) \hat{\mathcal{A}} | \Phi_{i \to a}^A \Phi_0^B \rangle}{\langle \Phi_0^A \Phi_0^B | \hat{\mathcal{A}} | \Phi_0^A \Phi_0^B \rangle}$$
$$= \Omega_{ia} = \sum_{i'} \tilde{B}_{i'a} D_{ii'} + \sum_j \tilde{A}_{ja} D_{ij}$$
$$+ \sum_{i'} \sum_j \sum_s \widetilde{\langle i'j || as \rangle} (D_{ii'} D_{sj} - D_{ij} D_{si'}). \quad (23)$$

The modified one- and two-electron matrix elements occurring in this expression correspond to a replacement of the virtual orbital χ_a with a modified virtual orbital $\tilde{\chi}_a = \chi_a - \sum_r \chi_r T_{ra}$. Similar equations can be derived for the matrix elements stemming from $\Psi_{\text{ind,B}}^{(1)}$. With these, one obtains $E_{\text{Ind}}^{(2)} = \sum_{ia} C_{ia} \Omega_{ia} + \sum_{jb} C_{jb} \Omega_{jb}$, from which the second-order exchange-induction energy is finally obtained through subtraction of $E_{\text{ind}}^{(2)}$.

3 Implementation and computational details

The above formalism in a spin-summed closed-shell form has been implemented into the SAPT routines of a development version of the MOLPRO program [43]. The program has been checked by comparing matrix elements as determined with the above formalism to the outcome of a simple test program in which the matrix elements were evaluated from explicit permutation of orbital products. Clearly, due to the factorial increase of the latter method this is only possible for cases with few electrons, such as He_2 and HeBe. In contrast, the formalism of Sect. 2 is much more efficient: as it stands, it scales no worse than N^5, where N is a measure of the system size. This is also the formal scaling behavior of the expression for the S^2-approximated exchange-induction energy as derived in [11]. Steps scaling as N^5 are the transformation of two-electron integrals over atomic orbital (AO) basis functions to integrals over molecular orbitals (MOs) and the preparation of the modified two-electron integrals according to Eq. (22). The latter can alternatively be generated by slightly modified two-

electron integral transformation routines using pseudo-MO coefficients for the modified virtual orbital $\tilde{\chi}_a$. The unmodified two-electron integrals can also be employed in the CPHF equations to determine the coefficients C_{ia}. Solution of the CPHF equations scales like N^6. Thus, the numerical effort for the calculation of $E_{\mathrm{Ind}}^{(2)}$ becomes negligible with increasing N. Starting from a set of appropriately transformed two-electron integrals, note that the effort for the calculation of all matrix elements (23) scales only like N^4 due to the possibility of contracting two indices of the two-electron integrals with D_{sj} and $D_{si'}$, respectively.

Clearly, there is room for improvements of the scaling behavior. Transforming the CPHF coefficients C_{ia} to a direct representation in terms of AO basis functions χ_μ, an operation that scales like N^3, one can use them directly in a contraction with matrix elements $\Omega_{\mu\nu}$. The latter, formally also obtained by transforming Ω_{ia} to the AO basis, can be directly calculated in steps scaling at most like N^4 from AO two-electron integrals and appropriate transformations of the inverse overlap matrices $\mathbf{D}$, in a way similar to that given for S^2-expanded exchange-induction energies in Eq. (14) of Ref. [19]. Furthermore, one could make use of density-fitting (or resolution-of-the-identity) approximations, which would bring the scaling of the CPHF procedure down to N^5 [19]. For the purpose of this paper, however, we focused our attention on simplicity of the code rather than on utmost efficiency.

For the Ar–HF complex, we considered linear geometries with the hydrogen atom pointing toward Ar. The H–F bond distance was fixed to 0.9169 Å, and interaction energies were computed as a function of the Ar–H distance $r_{\mathrm{Ar–H}}$. The geometry of the water monomer is characterized by an H–O bond distance of 0.9716 Å and a H–O–H angle of 104.69°. The relative orientation of the water molecules was chosen close to that of the C_s-symmetrical equilibrium geometry of the dimer [44], fixing the O–H–O angle of the hydrogen-bridge atoms at 170.04° and varying the intermolecular O–H distance $r_{\mathrm{O–H}}$. We used the aug-cc-pVQZ basis set (from here on denoted as aVQZ) of Dunning and coworkers in most of our calculations, and, in addition, for LiF also the aug-cc-pCVQZ basis set (from here on denoted as aCVQZ) [45–49]. With these basis sets, we also determined the position r_{m} of the minima (negative interaction energies) of the CP-corrected CCSD(T) potential energy curves and the distances σ where these curves cross the line of zero interaction energy before they become positive. Note that our use of the symbols r_{m} and σ corresponds to their usual meaning in the Lennard-Jones potential energy expression. The corresponding results are collected in Table 1. In the case of LiF—where the interatomic distances are particularly small—they were

Table 1 Zero-energy, σ, and minimum distances, r_{m}, [in Å] from CP-corrected CCSD(T)/aVQZ (and from CCSD(T)/aCVQZ for LiF)

	σ	r_{m}
Ne$_2$	2.82	3.13
Ar–HF	2.21	2.56
(H$_2$O)$_2$	1.51	1.96
HeCl$^-$	2.35	4.02
NeNa$^+$	2.18	2.53
LiF	1.00	1.57

obtained with the aCVQZ basis set correlating all electrons, while only the valence electrons were correlated in all other cases.

4 Results and discussion

Let us first discuss the quality of the S^2-approximation as a function of the intermolecular distance for the various systems investigated here. Figure 1 presents the ratios $E_{\mathrm{exch}}^{(1)}(S^2)/E_{\mathrm{exch}}^{(1)}$ and $E_{\mathrm{exch-ind}}^{(2)}(S^2)/E_{\mathrm{exch-ind}}^{(2)}$ for two fairly different cases, that is, the neon and the water dimers. The vertical lines on the r.h.s. in the diagrams of Fig. 1 represent the minimum r_{m} (cf. Table 1) of the neon-neon and the intermolecular oxygen-hydrogen distances, respectively. The region of distances larger than r_{m} will be denoted as "attractive well region" in the following. The vertical lines on the l.h.s. represent the zero-energy distances σ of Table 1. Distances between σ and r_{m} belong to the "repulsive well region". Finally, the range of distances smaller than σ with an exponentially growing interaction energy will be denoted as "wall region". For Ne$_2$, differences of the S^2-approximated first- and second-order exchange contributions are hardly perceptible in the attractive and repulsive well regions. They become significant only inside the wall region for fairly small distances. We note, however, that the relative errors introduced by the S^2-approximation are much more significant for the second-order exchange-induction energy than for the first-order exchange energy. This is also observed for the case of the water dimer–but here already in the attractive well region. In the repulsive well region, the magnitude of the errors rapidly grows with decreasing distance: for the first-order energy from less than 1 % at r_{m} to about 3 % at σ and for the second-order exchange-induction energy from less than 2 % to nearly 7 %. At a distance of 1.36 Å, corresponding to 0.9σ, the errors for $E_{\mathrm{exch}}^{(1)}$ and $E_{\mathrm{exch-ind}}^{(2)}$ amount to about -4 and -11 %, respectively.

The water dimer is not an exceptional case, as can be seen from Table 2 that presents the percentage deviations
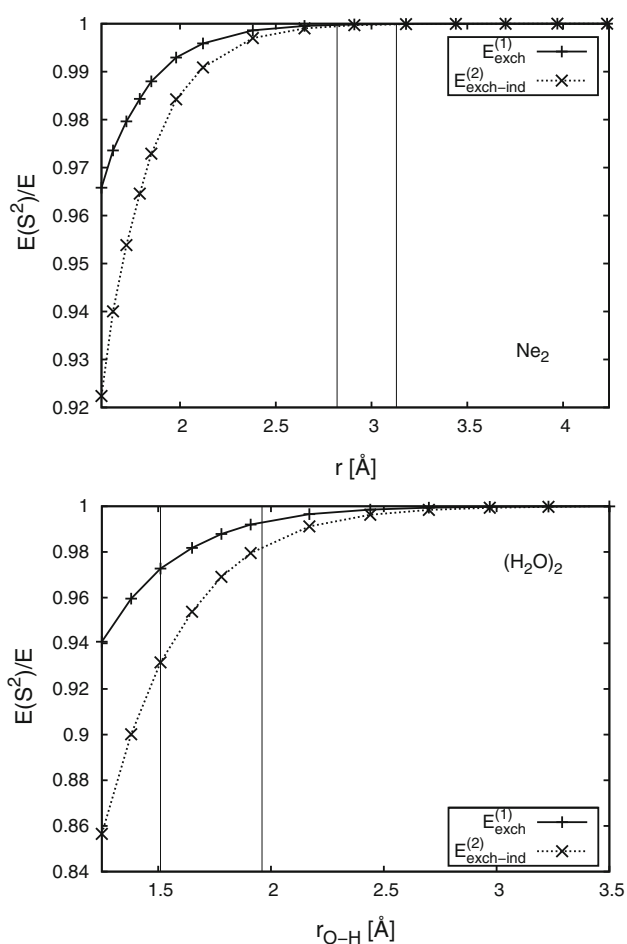
Fig. 1 Ratio of S^2-approximated, $E(S^2)$, to non-expanded, E, first-order exchange and second-order exchange-induction HF-SAPT/aVQZ energies for Ne_2 (*upper diagram*) and $(H_2O)_2$ (*lower diagram*). *Vertical lines* mark σ and r_m, respectively

of the S^2-approximated from the exact exchange energy contributions at 0.9σ, σ, and r_m for all systems investigated here. In the neighborhood of σ, the case of $HeCl^-$ is comparable to that of water, though the deviations at r_m are negligible due to the large minimum distance for this complex containing an extended anion. The extreme case is Li^+F^-, where the S^2-approximated $E^{(2)}_{exch-ind}$ reproduces only two-thirds of the exact value at σ. The cases of Ar-HF and $NeNa^+$, on the other hand, are more comparable to the case the neon dimer, with errors of at most 1 % throughout the entire well region for both, the first- and the second-order exchange contributions. Let us note, however, that for all of the investigated systems and throughout the entire distance range, (i) the exchange contributions are always positive, (ii) S^2-approximated values are always smaller than the exact ones, and (iii) the S^2-approximation is significantly worse for $E^{(2)}_{exch-ind}$ than for $E^{(1)}_{exch}$ (cf. Fig. S1 and Tables S1–S7 of Online Resource 1). In view of the last point, caution should be applied as to conclusions on the

Table 2 Deviations [in %] of S^2-approximated to exact $E^{(1)}_{exch}$ (in each first line) and $E^{(2)}_{exch-ind}$ (in each second line) at 0.9σ, σ, and r_m

	$0.9\,\sigma$	σ	r_m
Ne_2	−0.07	−0.02	−0.01
	−0.15	−0.05	−0.01
Ar-HF	−0.83	−0.41	−0.12
	−2.00	−1.01	−0.31
$(H_2O)_2$	−4.32	−2.73	−0.68
	−10.63	−6.84	−1.75
$HeCl^-$	−3.08	−1.59	−0.02
	−9.26	−4.79	−0.05
$NeNa^+$	−0.38	−0.15	−0.03
	−0.83	−0.30	−0.05
LiF	−18.73	−13.03	−1.68
	−48.29	−33.53	−3.80

validity of the S^2-approximation based on first-order results alone.

On the other hand, the first-order exchange contribution in general is larger than the second-order exchange-induction contribution, as shown in Table 3. For example, at 0.9σ the former is roughly two to five times larger. Nevertheless, that does not mean that the errors in $E^{(2)}_{exch-ind}$ could be neglected: since the latter at 0.9σ are a factor of two to three larger than the errors in $E^{(1)}_{exch}$ (cf. Table 2), the total errors are in the same order of magnitude. Fig. 2 directly compares the S^2-approximated interaction energies to their non-approximated counterparts for the examples of the neon and the water dimers. Please remember that interaction energies considered here do not contain the dispersion and exchange-dispersion contributions, which means that (i) no minimum is observed for the dispersion-bound neon dimer and that (ii) for the water dimer, the minimum is found at a larger distance than the

Table 3 Non-approximated energy contributions [in kJ/mol] $E^{(1)}_{exch}$ (in each first line) and $E^{(2)}_{exch-ind}$ (in each second line) at 0.9σ, σ, and r_m

	$0.9\,\sigma$	σ	r_m
Ne_2	4.329	1.213	0.271
	1.085	0.264	0.050
Ar-HF	36.60	16.30	4.148
	13.81	5.40	1.114
$(H_2O)_2$	239.0	138.9	27.92
	87.2	44.6	6.58
$HeCl^-$	132.0	64.21	0.611
	23.6	10.20	0.089
$NeNa^+$	37.00	12.66	2.027
	21.78	7.51	1.287
LiF	2,648	1,703	178.3
	999	694	136.5

minimum extracted from CCSD(T)/aVQZ which is indicated in the figure as a vertical line. In view of the discussion in the preceding paragraphs, the differences in the performance of the S^2-approximation for the two systems can hardly be surprising: for Ne$_2$ the S^2-approximation is excellent even for large portions of the wall region, while for the water dimer, significant deviations from the exact values are already seen in the repulsive well region. Fig. S2 of Online Resource 1 demonstrates that the latter is also the case for LiF, while Ar-HF and NeNa$^+$ are more comparable to Ne$_2$ in this respect. While in the case of HeCl$^-$, the S^2-approximation performs well in the entire well region, in the wall region a peculiarity is observed: at an interatomic distance of about 1.5 Å, that is, at about two-thirds of σ, the S^2-approximated energy shows a maximum. This is an obvious failure of the S^2-approximation in a distance region where the non-approximated interaction energy shows the expected exponential increase.
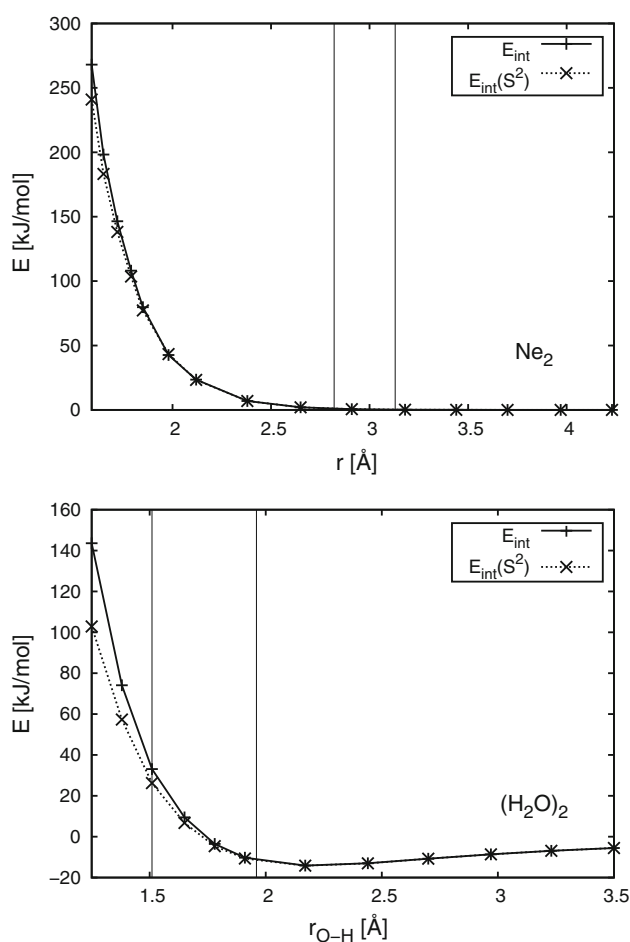
The consequences of various stages of the S^2-approximation on $\delta(HF)$ values obtained with them are exemplified in Fig. 3. Approximating both $E_{exch}^{(1)}$ and $E_{exch-ind}^{(2)}$, we start to see differences to the exact value already at the minimum distance of the water dimer, and only 67 % of the exact value is reproduced at the zero-energy distance σ. This improves when only $E_{exch-ind}^{(2)}$ is approximated: now 86 % of the exact value are reproduced at σ. On the other hand, since the magnitude of $\delta(HF)$ is larger than that of its approximations, calculating E_{int} with S^2-approximated HF-SAPT yields results that are closer to the CP-corrected supermolecular HF interaction energies over the entire range of distances considered here. Nevertheless, the observation that in one of the approximations $\delta(HF)$ attains a minimum at an O-H distance of about 1.4 Å is suspicious. In fact, for the neon dimer, where one has to look deep inside the wall region to see noticeable differences between the exact and the approximated $\delta(HF)$ values, one finds minima for both approximations - and in particular the
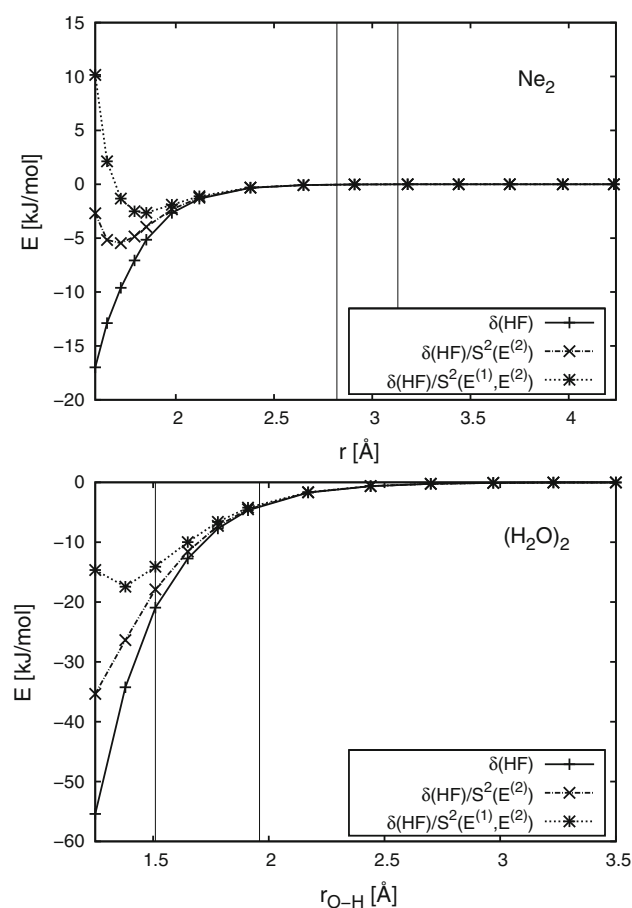

Fig. 2 Non-expanded, E_{int}, and S^2-approximated, $E_{int}(S^2)$, HF-SAPT/aVQZ interaction energies for Ne$_2$ (upper diagram) and (H$_2$O)$_2$ (lower diagram). Vertical lines mark σ and r_m, respectively

Fig. 3 The $\delta(HF)$ correction as determined from non-expanded first- and second-order energies, using S^2-approximated second-order only, $\delta(HF)/S^2(E^{(2)})$, and using S^2-approximated first- and second-order contributions, $\delta(HF)/S^2(E^{(1)},E^{(2)})$, for Ne$_2$ (upper diagram) and (H$_2$O)$_2$ (lower diagram). Vertical lines mark σ and r_m, respectively

example of the "full" approximation for both $E_{\text{exch}}^{(1)}$ and $E_{\text{exch-ind}}^{(2)}$ demonstrates that for very small interatomic distances, the approximated values will become larger in magnitude than the exact value. Furthermore, one observes a change of sign in the approximated values with decreasing distance, whereas the non-approximated δ(HF) displays a monotonic behavior. As demonstrated in Fig. S3 of Online Resource 1, this is also the case for most of the other systems considered. Again, the case of LiF is a more extreme variant of that of the water dimer, while Ar-HF and HeCl⁻ resemble Ne₂. A somewhat exceptional case is that of NeNa⁺, where even the non-approximated δ(HF) correction attains positive values in the repulsive wall region, while it is negative in all other cases. This is most likely due to a missing third-order energy contribution in our HF-SAPT E_{int}: while in a point-multipole model of the atom-ion interaction such a third-order term does not occur, it is present in SAPT due to the full consideration of atomic charge distributions and charge-density response functions [39, 40]. As a third-order contribution, its sign should be sensitive to the sign of an overall charge on one (or both) of the interacting monomers, so that one would expect a differing sign for it when comparing NeNa⁺ with HeCl⁻.

Third-order SAPT induction contributions have recently been implemented by Patkowski, Szalewicz, and Jeziorski and compared to the δ(HF) higher-order induction contributions estimate [39, 40]. It was found that the sum of the third-order induction plus exchange-induction contributions differs significantly from δ(HF) at the equilibrium geometries of some neutral intermolecular complexes, while for large intermolecular separations, excellent agreement was observed when orbital relaxation effects were taken into account. The second- and third-order exchange-induction energies calculated by Patkowski et al. were obtained within the S^2-approximation. As shown above, with the S^2-approximation for the second-order exchange-induction energy, the magnitude of δ(HF) in general is underestimated, if it is a negative number, as was the case for all systems considered in Refs. [39, 40]. Since in the examples given there, the sum of the third-order induction plus exchange-induction contributions always represents only a fraction of δ(HF), the disagreement becomes even larger when compared to the non-approximated δ(HF). For example, the sum of the third-order contributions was found to be −1.30 kJ/mol at the equilibrium geometry of the water dimer, while δ(HF) is given as −3.42 kJ/mol in Ref. [40]. The latter value is in good agreement with our two different S^2-approximations which yield −3.54 (approximation for first and second order) and −3.73 kJ/mol (only second order approximated), respectively, for our somewhat different (H₂O)₂ equilibrium geometry. Our non-approximated δ(HF) correction finally

amounts to −3.84 kJ/mol. Very recently Lao and Herbert have expounded that the third-order exchange-induction contribution for induction-dominated dimers seems to be dramatically underestimated with the S^2-approximation at short intermolecular distances [50] and have recommended to alternatively use the δ(HF) correction for determining full potential energy curves. Our results explicitly support their conclusion that going beyond the S^2-approximation is even more important for higher-order than for first-order exchange contributions. Furthermore, the observation that eliminating the underestimation of the third-order exchange-induction energy would lead to an even larger discrepancy with δ(HF) at the equilibrium geometry of the water dimer indicates that fourth- and even higher-order induction and exchange-induction contributions become significant here. This is another reason to support the finding [50] that calculation of δ(HF) cannot be avoided even if third-order results are available.

As a final point, let us comment on the importance of core-polarization for the exchange contributions. This was investigated for the case of the LiF molecule since we expected effects of core-polarization to be most visible in this case due to the small values for r_m and σ found here. Even when the aCVQZ basis set, strictly speaking, was designed to account for core-valence electron correlation rather than for core-polarization, a comparison of the HF-SAPT energy contributions determined with it to those from the aVQZ basis set will give us valuable hints: in fact, it was found that for distances smaller than 3.0 Å, all SAPT contributions deviate by 0.5 % at most (cf. Tables S6 and S7 of Online Resource 1). Interestingly, the induction energy is the only contribution that starts to deviate by more than a percent for larger interatomic distances, indicating that the polarizabilities are influenced by the presence of the core-valence correlation functions in the basis set. The strongest influence of the basis set is found for total interaction energies in the neighborhood of σ, of course, where the individual energy contributions cancel out. At larger r, on the other hand, the total interaction energies agree very well due to the increasing dominance of the electrostatic interaction between the ions with increasing distance.

5 Conclusions and outlook

In summary, we have derived and implemented an approach to evaluate second-order exchange-induction SAPT energies for single-determinant monomer wavefunctions, which is correct to all orders of the intermonomer overlap S, that is, taking multiple electron exchange between the monomers into account. The approach can be formulated such that it scales with the fourth power of the

system size, once the coupled-perturbed Hartree-Fock coefficients determining linear response of the ground state are available. We have used the method to investigate the performance of the S^2- or single-exchange-approximation to $E_{exch-ind}^{(2)}$ at the HF-SAPT level. For all of our test systems and all distances between them, it was found that the errors introduced by the S^2-approximation are more pronounced in $E_{exch-ind}^{(2)}$ than in $E_{exch}^{(1)}$, typically by factors of two to three. The S^2-approximation systematically leads to an underestimation of the invariably positive exact exchange contributions. While this underestimation is below 1 % and thus negligible throughout the entire well regions of Ne_2, Ar-HF, and $NeNa^+$, it exceeds a few percent in the repulsive part of the well regions of $(H_2O)_2$, $HeCl^-$, and Li^+F^-. In the repulsive wall region at small intermolecular distances, where the CCSD(T) interaction energies are positive, the deviations may become very significant: for LiF as our most extreme example, the S^2-approximated $E_{exch-ind}^{(2)}$ reproduces only about half of the exact value at a distance of 0.9 Å, that is, 90 % of the distance σ where the CCSD(T) potential energy curve starts to become positive. As a consequence, S^2-approximated HF-SAPT interaction energy curves are too shallow in the repulsive well and the wall regions, and this effect is already significant for the water dimer as a representative for hydrogen-bridged systems. Furthermore, the use of the S^2-approximation may have a notable effect on the calculated values of the $\delta(HF)$ estimate of higher-order induction and exchange-induction energies, as exemplified by the wall region of $HeCl^-$, $(H_2O)_2$, and LiF, and the repulsive well regions of the latter two systems. With the exception of $NeNa^+$, it was found that the non-approximated $\delta(HF)$ shows a monotonic behavior with decreasing distance while sign changes are observed when the S^2-approximation is employed for the first-order and/or second-order exchange contributions.

Clearly, the approach presented here can also be used in the framework of DFT-SAPT, employing the Kohn-Sham determinant and the linear coupled-perturbed Kohn-Sham perturbation wavefunction. Furthermore, it can be extended to exchange-dispersion energies. One should note that while DFT-SAPT is able to take intramonomer electron correlation effects on the non-exchange contributions into account in a potentially exact way, this is not the case for the exchange contributions [14]. Therefore, any DFT-SAPT variant can only be an approximation, and one has to test its quality. We have derived and implemented a DFT-SAPT method that includes non-expanded second-order exchange-dispersion energies and checked its performance by comparison to high-level CCSD(T) and some MB-SAPT results. This will be the topic of a forthcoming publication.

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