Theor Chem Acc (2010) 127:211–221
DOI 10.1007/s00214-010-0748-0

REGULAR ARTICLE

Orbital relaxation and the third-order induction energy in symmetry-adapted perturbation theory

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Received: 24 December 2009 / Accepted: 19 March 2010 / Published online: 17 April 2010
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Abstract Theoretical investigations of the induction interaction between closed-shell molecules which fully account for the orbital relaxation effects are presented. Explicit expressions for the third-order induction energy in terms of molecular integrals and orbital energies are given and implemented within the SAPT2008 program for symmetry-adapted perturbation theory (SAPT) calculations. Numerical investigations for the He–He, He–LiH, Ar–Ar, H_2–CO, H_2O–H_2O, and H_2O–NH_3 model dimers show that the orbital relaxation increases the third-order induction interaction by 15 to 50% at near-equilibrium geometries, with the largest effect observed for complexes involving highly polar monomers. At large intermonomer separations, the relaxed third-order induction energy perfectly recovers the difference $\delta E_{\rm int}^{\rm HF}$ between the Hartree–Fock interaction energy and the sum of the uncorrelated SAPT contributions through second order in the intermolecular interaction operator. At the near-equilibrium geometries, the sum of the relaxed third-order induction and exchange-induction energies reproduces, however, only a small fraction (6 to 15%) of $\delta E_{\rm int}^{\rm HF}$ for the nonpolar systems and about 40 to 60% for the polar ones. A comparison of the complete SAPT calculations with the coupled-cluster treatment with single, double, and noniterative triple excitations [CCSD(T)] suggests that the pure SAPT approach with all the available third-order corrections is more accurate for nonpolar systems while for the polar ones the hybrid approach including $\delta E_{\rm int}^{\rm HF}$ gives better results.

Keywords Intermolecular interactions · Symmetry-adapted perturbation theory · Induction energy

1 Introduction

Symmetry-adapted perturbation theory (SAPT) provides both the conceptual framework enabling one to understand weak intermolecular interactions and the computational apparatus allowing quantitative prediction of multidimensional intermolecular potential energy surfaces [1–4]. When a sufficiently large basis set is chosen for a considered system, the reliability and accuracy of SAPT calculations depends on two factors: (a) the adequacy of the treatment of intramonomer electron correlation and (b) the importance of the neglected third- and higher-order effects. Significant progress has recently been achieved in an accurate handling of intramonomer correlation, both at the first and at the second order in the intermolecular interaction operator V. For small systems, advanced coupled-cluster techniques are available to account for the intramonomer correlation contributions to the electrostatic [5, 6] and exchange interactions [7] in the first, and the induction [8] and dispersion energies [9] in the second order in V. For larger molecules, DFT techniques [10–17] can be used to efficiently treat the intramonomer correlation effects for the lowest-order interaction energy contributions.

Dedicated to the memory of Professor Jürgen Hinze and published as part of the Hinze Memorial Issue.

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With these recent developments, an adequate inclusion of the third- and higher-order energy components becomes increasingly important. Although in some cases, the SAPT treatment through second order may be quite accurate (the helium pair potential is a good example [18]), the few high-order SAPT studies performed thus far [19–22] clearly show that the third- and higher-order effects in SAPT are in general not negligible and have to be included as accuracy requirements increase.

Two procedures are currently employed to account for contributions beyond the second order. Most often, the genuine SAPT treatment is limited to the first and second order in V and higher-order effects are estimated at the Hartree–Fock level by adding the so-called "delta Hartree–Fock" correction $\delta E_{\mathrm{int}}^{\mathrm{HF}}$, defined as the difference between the conventional "supermolecular" Hartree–Fock interaction energy $E_{\mathrm{int}}^{\mathrm{HF}}$ and the sum of the first- and second-order SAPT contributions to $E_{\mathrm{int}}^{\mathrm{HF}}$ [23, 24]:

$$\delta E_{\mathrm{int}}^{\mathrm{HF}} = E_{\mathrm{int}}^{\mathrm{HF}} - E_{\mathrm{elst}}^{(10)} - E_{\mathrm{exch}}^{(10)} - E_{\mathrm{ind,resp}}^{(20)} - E_{\mathrm{exch-ind,resp}}^{(20)}, \quad (1)$$

where $E_{\mathrm{elst}}^{(10)}$ and $E_{\mathrm{exch}}^{(10)}$ are the electrostatic and exchange energies computed in SAPT with the complete neglect of intramonomer correlation [1] (this is reflected by the superscript 0), while $E_{\mathrm{ind,resp}}^{(20)}$ and $E_{\mathrm{exch-ind,resp}}^{(20)}$ are the induction and exchange-induction SAPT contributions computed neglecting the intramonomer correlation but with a proper account of the coupled Hartree–Fock-type *relaxation* (response) of each monomer to the static electric field of the interacting partner [25] (the relaxation effects are sometimes referred to as the "apparent correlation" [26]). The advantage of using this *hybrid* approach is the simplicity of the computational procedure and the fact that $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ includes induction (polarization-type) effects through infinite order in V. These high-order induction contributions are accounted for only approximately, i.e., with the neglect of true intramonomer correlation effects. More importantly, however, it is clear now that while all induction contributions recovered by the Hartree–Fock theory are physical [26], there exist short-range (exchange) contributions to $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ which cannot be interpreted as representing the true interaction energy. For instance, $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ contains spurious exchange terms of the zeroth order in V [27–29], which obviously cannot reflect the physics of the interaction. These zeroth-order exchange terms are very small [28], but there are also much larger terms of the first and second order in V, which are due to unphysical, exchange deformation of orbitals [24] and cannot be a part of the SAPT expansion of the interaction energy (the SAPT expansion, when carried out to sufficiently high order, can provide extremely accurate interaction energies without any exchange deformation of the wave function [19, 30–34]). Therefore, by using the hybrid approach described earlier, we are including in an uncontrollable way some unphysical, though hopefully small, contributions to the computed interaction energy.

A theoretically more appealing procedure is to extend SAPT to allow direct computation of third-order contributions. This approach, started already in the 1990s [35], was pursued in some detail in Ref. [36] where the third-order SAPT energy expression was derived assuming the complete neglect of the orbital relaxation and intramonomer correlation effects but including all intermonomer correlation (dispersion) and exchange contributions. Specifically, the third-order induction $E_{\mathrm{ind,}}^{(30)}$ dispersion $E_{\mathrm{disp}}^{(30)}$, and mixed induction-dispersion $E_{\mathrm{ind-disp}}^{(30)}$ contributions, together with the corresponding exchange corrections $E_{\mathrm{exch-ind}}^{(30)}$, $E_{\mathrm{exch-disp}}^{(30)}$, and $E_{\mathrm{exch-ind-disp}}^{(30)}$, were derived, coded (these corrections are available in the current release of the SAPT code [37]), and applied to a series of model dimers representing various strengths and types of interactions. The study of Ref. [36] has shown that for dispersion-bound dimers composed of nonpolar (or weakly polar) monomers (like the Ar_2 or H_2–CO complexes) the unphysical terms in $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ are significant relative to the total interaction energy and the hybrid approach should not be used. The pure SAPT approach, including the available third-order energy corrections, provides more accurate results in such cases. When the monomers are polar (like the water dimer or the ammonia–water complex) and the electrostatic and induction effects dominate, the unphysical terms in $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ appear to be less relevant than the high-order induction effects and the hybrid approach remains more accurate. Note that the mechanism of the induction interaction is quite different in the two types of systems. When both monomers are closed-shell atoms in their ground states, the induction interaction results exclusively from charge-overlap effects. When both monomers are strongly polar, it is mainly due to the classical polarization mechanism involving permanent and induced multipoles. For weakly polar systems, like H_2–CO, the charge-overlap effects dominate at short range, including the region of the van der Waals minimum. It was also observed [36] that $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ was substantially different from the sum $E_{\mathrm{ind}}^{(30)} + E_{\mathrm{exch-ind}}^{(30)}$. It was not clear, however, whether this difference was due to the fourth- and higher-order induction terms, to the orbital relaxation contributions to the third-order induction and exchange-induction energies, neglected in the development of Ref. [36], or to the spurious exchange terms in $\delta E_{\mathrm{int}}^{\mathrm{HF}}$. It has been conjectured [36] that the inclusion of the orbital relaxation in third order will further improve the accuracy of the pure SAPT treatment and will extend the class of systems for which the pure SAPT will perform better than the hybrid approach.

In this communication, we will verify the above-mentioned hypothesis by extending the development of Ref. [36] to include the orbital relaxation effects in the third-order induction energy. Similarly as in Ref. [36], we shall consider interactions of closed-shell systems only. In Sect. 2, we shall present a general formulation of the orbital relaxation in the induction interactions and derive a formula for the relaxed third-order induction energy. The exchange quenching of this quantity will be estimated from the unrelaxed values. Some details of the computational implementation of the derived equations and the numerical results of our calculations are given in Sect. 3. Section 4 presents conclusions and summary of our work.

2 Theory

The infinite-order induction (or polarization) energy in the interaction of two systems (monomers) A and B, described by the Hamiltonians H_{A} and H_{B}, is defined [1] as the minimum of the expectation value of the dimer Hamiltonian $H = H_{\mathrm{A}} + H_{\mathrm{B}} + V$ within a class of trial wave functions of the form $\Psi = \Psi_{\mathrm{A}}\Psi_{\mathrm{B}}$, where Ψ_{A} and Ψ_{B} are arbitrary (normalized) functions that depend on the coordinates of the N_{A} electrons assigned to monomer A, and on the coordinates of the N_{B} electrons assigned to B, respectively. Since this infinite-order induction energy may suffer from the so-called polarization collapse [38] and may not behave correctly at large intermonomer separations R, we shall only consider finite-order induction energies. These are defined by parametrizing the dimer Hamiltonian as $H = H_{\mathrm{A}} + H_{\mathrm{B}} + \lambda V$, expanding the resulting induction energy in powers of λ, taking the nth order term in this expansion and, finally, setting $\lambda = 1$.

The above definition obviously neglects the *intermonomer* electron correlation (dispersion) but takes full account of the *intramonomer* true electron correlation as well as all orbital relaxation effects. If the trial functions Ψ_{A} and Ψ_{B} are restricted to a single-determinantal form, as suggested some time ago by Sadlej [26], the intramonomer true correlation effects are obviously neglected, but the relaxation effects remain fully recovered. The relaxed induction energies considered in this work are thus defined by the power series expansion (in λ) of the minimum of the expectation value of $H = H_{\mathrm{A}} + H_{\mathrm{B}} + \lambda V$, with trial functions in the form of a product of normalized Slater determinants Ψ_{A} and Ψ_{B} , depending on the coordinates of electrons assigned to A and B, respectively. It is convenient to parametrize the arbitrary determinants Ψ_{A} and Ψ_{B} by means of anti-Hermitian operators A and B which generate (via exponentiation) unitary transformations of spin-orbitals occupied in the (unperturbed) Hartree–Fock determinants Φ_{A} and Φ_{B} of free monomers:

$$\Psi_{\mathrm{A}} = \mathrm{e}^{A}\Phi_{\mathrm{A}}, \quad \Psi_{\mathrm{B}} = \mathrm{e}^{B}\Phi_{\mathrm{B}} \tag{2}$$

In view of the theorem proved by Rowe et al. [39], A and B can be expressed (up to irrelevant purely imaginary additive constants) through a set of nonredundant parameters C^{α}_{ρ} and C^{β}_{σ} defining single-excitation operators

$$C_{\mathrm{A}} = C^{\alpha}_{\rho}a^{\rho}a_{\alpha}, \quad C_{\mathrm{B}} = C^{\beta}_{\sigma}b^{\sigma}b_{\beta} \tag{3}$$

such that

$$A = C_{\mathrm{A}} - C^{\dagger}_{\mathrm{A}}, \quad B = C_{\mathrm{B}} - C^{\dagger}_{\mathrm{B}}. \tag{4}$$

In Eq. (3), and throughout the rest of the paper, the operators a^{κ} and a_{μ} (b^{λ} and b_{ν}) denote the standard creation and annihilation operators, respectively, acting on the spin-orbitals spanning the basis set for monomer A (B). The Greek letters α and ρ, with or without any additional super- and sub-scripts, are used to label spin-orbitals that are occupied and unoccupied (virtual), respectively, in the reference determinant Φ_{A}. An analogous convention holds for the indexes β, σ and the monomer B. Finally, summation over repeated *lower and upper* indices is implied in Eq. (3) and throughout the text. All operators a^{κ} and a_{μ} commute with all operators b^{λ} and b_{ν} since these two sets of operators act in different Fock spaces [35]. Therefore, the operators A and B must also commute, $[A, B] = 0$.

The induction energy is now obtained by minimizing the functional

$$J(A,B) = \langle \Psi_{\mathrm{A}}\Psi_{\mathrm{B}}|H\Psi_{\mathrm{A}}\Psi_{\mathrm{B}}\rangle = \langle \mathrm{e}^{-A-B}H\mathrm{e}^{A+B}\rangle \tag{5}$$

with respect to the parameters C^{α}_{ρ} and C^{β}_{σ}. In Eq. (5) and in the following text, we use the notation

$$\langle X\rangle \equiv \langle \Phi_{\mathrm{A}}\Phi_{\mathrm{B}}|X\Phi_{\mathrm{A}}\Phi_{\mathrm{B}}\rangle \tag{6}$$

for any operator X. The operators A and B minimizing the functional $J(A, B)$ are obtained from equations

$$\left(\frac{\partial}{\partial\eta}J(A+\eta\delta A,B)\right)_{\eta=0} = 0, \tag{7}$$

and

$$\left(\frac{\partial}{\partial\eta}J(A,B+\eta\delta B)\right)_{\eta=0} = 0, \tag{8}$$

satisfied for arbitrary operator variations $\delta A = \delta C_{\mathrm{A}} - \delta C^{\dagger}_{\mathrm{A}}$ and $\delta B = \delta C_{\mathrm{B}} - \delta C^{\dagger}_{\mathrm{B}}$. Using the nested commutator expansion $e^{-X}He^{X} = H + [H,X] + [[H,X],X]/2! + \cdots$ one can write the variational conditions of Eqs. (7) and (8) in the expanded form

$$\langle [H,\delta A]\rangle + \langle [[H,\delta A],A]\rangle + \langle [[H,\delta A],B]\rangle + \cdots = 0 \tag{9}$$

and

$$\langle [H,\delta B]\rangle + \langle [[H,\delta B],B]\rangle + \langle [[H,\delta B],A]\rangle + \cdots = 0, \tag{10}$$

where the terms not written out explicitly originate from triple and higher commutators. To arrive at Eqs. (9) and (10), we used the identities

$$\langle[[H,\delta A],A]\rangle = \langle[[H,A],\delta A]\rangle \quad \text{and} \quad \langle[[H,\delta B],B]\rangle = \langle[[H,B],\delta B]\rangle, \tag{11}$$

which in turn stem from the Jacobi identity $[[X, Y], Z] + [[Y, Z], X] + [[Z, X], Y] = 0$ and the fact that $\langle[[A, \delta A], H]\rangle = 0$ since Φ_A is an eigenfunction of $[A, \delta A]$.

Equations (9) and (10) are transcendental and cannot be solved exactly. To obtain a perturbation theory solution, the only one we are interested in, we parametrize H as $H_0 + \lambda V$, where $H_0 = H_A + H_B$, and expand the operators A and B in powers of λ:

$$A = A^{(0)} + \lambda A^{(1)} + \lambda^2 A^{(2)} + \cdots,$$
$$B = B^{(0)} + \lambda B^{(1)} + \lambda^2 B^{(2)} + \cdots. \tag{12}$$

After expanding Eqs. (9) and (10) in powers of λ, we find that the resulting zeroth-order equations are formally identical to Eqs. (9) and (10), but with the operators $H, A,$ and B replaced, respectively, by $H_0, A^{(0)}$, and $B^{(0)}$. When the determinants Φ_A and Φ_B fulfill the monomer Hartree–Fock equations, $\langle[H_0, \delta A]\rangle$ and $\langle[H_0, \delta B]\rangle$ vanish according to the Brillouin theorem, and the inhomogeneities in Eqs. (9) and (10) disappear. Thus, the zeroth-order equations are satisfied by setting $A^{(0)} = 0$ and $B^{(0)} = 0$. With this zeroth-order solution, all subsequent higher-order equations are finite.

When $A^{(0)} = B^{(0)} = 0$, the first-order equations are

$$\langle[V,\delta A]\rangle + \langle[[H_0,A^{(1)}],\delta A]\rangle + \langle[[H_0,B^{(1)}],\delta A]\rangle = 0, \tag{13}$$

$$\langle[V,\delta B]\rangle + \langle[[H_0,B^{(1)}],\delta B]\rangle + \langle[[H_0,A^{(1)}],\delta B]\rangle = 0. \tag{14}$$

The last terms on the l.h.s. of Eqs. (13) and (14) must vanish since if one substitutes $H_0 = H_A + H_B$, each resulting term contains two operators acting on the functions of one monomer (A or B) and one operator that acts on the functions of the other monomer and commutes with the previous two. After this simplification, Eq. (13) can be written as

$$2\mathrm{Re}\langle\delta A|V + [H_0,A^{(1)}]\rangle = 0, \tag{15}$$

or, when $A^{(1)}$ is replaced by $C_A^{(1)} - C_A^{(1)\dagger}$, as

$$2\mathrm{Re}\langle\delta C_A|\Omega_B + [H_A, C_A^{(1)} - C_A^{(1)\dagger}]\rangle_A = 0, \tag{16}$$

where $\langle X|Y\rangle$ and $\langle X|Y\rangle_A$ are shorthand notations for $\langle X\Phi_A\Phi_B|Y\Phi_A\Phi_B\rangle$ and $\langle X\Phi_A|Y\Phi_A\rangle$, respectively (analogously, $\langle\Phi_A|X\Phi_A\rangle$ will be denoted by $\langle X\rangle_A$). The operator Ω_B is defined as

$$\Omega_B = \langle\Phi_B|V\Phi_B\rangle = \sum_{i\in A}^{N_A} \omega_B(\mathbf{r}_i), \tag{17}$$

where $\omega_B(\mathbf{r}_i)$ represents the electrostatic potential generated by the Hartree–Fock monomer B. Similar equation, involving Ω_A, holds for $C_B^{(1)}$. From now on, we shall assume that all orbitals are real so the real part symbol Re in Eq. (16) can be dropped. Equation (16) becomes then identical with the equation determining the Coupled Perturbed Hartree–Fock (CPHF) coefficients [40] describing the linear response of a Hartree–Fock molecule A to an external (real) potential $\omega_B(\mathbf{r})$. Thus, the first-order component of the operator C_A is equal to the standard CPHF operator. The same conclusion regarding C_B can be derived from Eq. (14). As will be shown below, Wigner's $2n + 1$ rule applies in the perturbation approach presented here, so the knowledge of A and B through first order in V is sufficient to obtain the induction energy through third order. Therefore, we will not consider the second- and higher-order contributions to A and B any further.

The relaxed induction energies of a given order in V are obtained by expanding $J(A, B)$, Eq. (5), in powers of λ. In the second order, one obtains

$$J^{(2)} = \langle[H_0, A^{(2)} + B^{(2)}]\rangle + \frac{1}{2}\langle[[H_0, A^{(1)} + B^{(1)}], A^{(1)} + B^{(1)}]\rangle + \langle[V, A^{(1)} + B^{(1)}]\rangle. \tag{18}$$

The first term in Eq. (18) is zero due to the Brillouin theorem, and the "mixed" parts (including simultaneously $A^{(1)}$ and $B^{(1)}$) of the second term vanish for the same reasons as the last terms in Eqs. (13) and (14). Moreover, the first-order equation, Eq. (13), implies that $\langle[[H_0, A^{(1)}], A^{(1)}]\rangle = -\langle[V, A^{(1)}]\rangle$ so that the second term in Eq. (18) cancels with one half of the last one. Thus,

$$J^{(2)} = \langle VC_A^{(1)}\rangle + \langle VC_B^{(1)}\rangle. \tag{19}$$

This expression for $J^{(2)}$ is identical to the one for the relaxed second-order induction correction $E^{(20)}_{\mathrm{ind,resp}}$ [25, 41]. Thus, as expected, our approach recovers the second-order induction energy with a full account of the orbital relaxation effects.

The third-order component of Eq. (5) is

$$\begin{aligned} J^{(3)} = {} & \langle[H_0, A^{(3)} + B^{(3)}]\rangle + \langle[V, A^{(2)} + B^{(2)}]\rangle \\ & + \langle[[H_0, A^{(1)} + B^{(1)}], A^{(2)} + B^{(2)}]\rangle \\ & + \frac{1}{2}\langle[[V, A^{(1)} + B^{(1)}], A^{(1)} + B^{(1)}]\rangle \\ & + \frac{1}{6}\langle[[[H_0, A^{(1)} + B^{(1)}], A^{(1)} + B^{(1)}], A^{(1)} + B^{(1)}]\rangle \end{aligned} \tag{20}$$

(note that $\langle[[H_0, A^{(1)} + B^{(1)}], A^{(2)} + B^{(2)}]\rangle = \langle[[H_0, A^{(2)} + B^{(2)}], A^{(1)} + B^{(1)}]\rangle$ in direct analogy to Eq. (11)). Just like for $J^{(2)}$, the term involving $A^{(3)} + B^{(3)}$, as well as the "mixed" terms, involving simultaneously H_0, $A^{(k)}$, and $B^{(l)}$, are zero. If one substitutes $\delta A = A^{(2)}$ and $\delta B = B^{(2)}$ into Eqs. (13) and (14), respectively, one finds that the two terms involving $A^{(2)}$ or $B^{(2)}$ in Eq. (20) add up to zero.

Thus, $J^{(3)}$ is expressible by $A^{(1)}$ and $B^{(1)}$ alone, in accordance with Wigner's $2n+1$ rule:

$$J^{(3)} = \frac{1}{6}\langle[[[H_{\mathrm{A}}, A^{(1)}], A^{(1)}], A^{(1)}]\rangle_{\mathrm{A}} + \frac{1}{6}\langle[[[H_{\mathrm{B}}, B^{(1)}], B^{(1)}], B^{(1)}]\rangle_{\mathrm{B}} + \frac{1}{2}\langle[[V, A^{(1)} + B^{(1)}], A^{(1)} + B^{(1)}]\rangle, \tag{21}$$

or, equivalently,

$$J^{(3)} = \frac{1}{3}\langle C_{\mathrm{A}}^{(1)}|[[H_{\mathrm{A}}, A^{(1)}], A^{(1)}]\rangle_{\mathrm{A}} + \frac{1}{3}\langle C_{\mathrm{B}}^{(1)}|[[H_{\mathrm{B}}, B^{(1)}], B^{(1)}]\rangle_{\mathrm{B}} + \langle C_{\mathrm{A}}^{(1)} + C_{\mathrm{B}}^{(1)}|[V, A^{(1)} + B^{(1)}]\rangle, \tag{22}$$

where we have used the fact that

$$C_{\mathrm{A}}^{(1)\dagger}\Phi_{\mathrm{A}} = 0 \quad \text{and} \quad C_{\mathrm{B}}^{(1)\dagger}\Phi_{\mathrm{B}} = 0. \tag{23}$$

After expanding the double commutator, the first term of Eq. (22) can be written as

$$\frac{1}{3}\left\langle C_{\mathrm{A}}^{(1)}\middle|H_{\mathrm{A}}\left(C_{\mathrm{A}}^{(1)}\right)^2 - H_{\mathrm{A}}C_{\mathrm{A}}^{(1)\dagger}C_{\mathrm{A}}^{(1)} - 2C_{\mathrm{A}}^{(1)}H_{\mathrm{A}}C_{\mathrm{A}}^{(1)} + 2C_{\mathrm{A}}^{(1)\dagger}H_{\mathrm{A}}C_{\mathrm{A}}^{(1)} + \left(C_{\mathrm{A}}^{(1)} - C_{\mathrm{A}}^{(1)\dagger}\right)^2 H_{\mathrm{A}}\right\rangle_{\mathrm{A}}. \tag{24}$$

Now, the second, third, and fifth terms in the ket part of the expression (24) give zero contributions because $H_{\mathrm{A}}\Phi_{\mathrm{A}}$ is orthogonal to the space of single or triple excitations from Φ_{A}. The contribution of the fourth term is exactly twice as large as that of the first one. Thus, the first term in Eq. (22) simplifies to the following form

$$\langle C_{\mathrm{A}}^{(1)}|H_{\mathrm{A}}(C_{\mathrm{A}}^{(1)})^2\rangle_{\mathrm{A}} = \langle C_{\mathrm{A}}^{(1)}|W_{\mathrm{A}}(C_{\mathrm{A}}^{(1)})^2\rangle_{\mathrm{A}}, \tag{25}$$

where W_{A} is the intramonomer correlation operator defined as (the Møller–Plesset partition) the difference between the total monomer Hamiltonian H_{A} and the Fock operator F_{A} for this monomer (F_{A} is diagonal in the determinantal basis used by us so that $\langle C_{\mathrm{A}}^{(1)}|F_{\mathrm{A}}(C_{\mathrm{A}}^{(1)})^2\rangle_{\mathrm{A}} = 0$). Analogously, the second term in Eq. (22) reduces to $\langle C_{\mathrm{B}}^{(1)}|W_{\mathrm{B}}(C_{\mathrm{B}}^{(1)})^2\rangle_{\mathrm{B}}$.

The last term in Eq. (22), equal to

$$\langle C_{\mathrm{A}}^{(1)} + C_{\mathrm{B}}^{(1)}|V(C_{\mathrm{A}}^{(1)} + C_{\mathrm{B}}^{(1)}) + (C_{\mathrm{A}}^{(1)\dagger} - C_{\mathrm{A}}^{(1)} + C_{\mathrm{B}}^{(1)\dagger} - C_{\mathrm{B}}^{(1)})V\rangle, \tag{26}$$

cannot be simplified as much as the previous two. The contributions $\langle C_{\mathrm{A}}^{(1)}|C_{\mathrm{A}}^{(1)\dagger}V\rangle$ and $\langle C_{\mathrm{B}}^{(1)}|C_{\mathrm{B}}^{(1)\dagger}V\rangle$ vanish because V cannot produce a double excitation on any monomer. Moreover,

$$\langle C_{\mathrm{B}}^{(1)}|C_{\mathrm{A}}^{(1)}V\rangle = \langle C_{\mathrm{A}}^{(1)}|C_{\mathrm{B}}^{(1)}V\rangle = 0 \tag{27}$$

because of Eq. (23). With these simplifications, the final formula for the relaxed third-order induction energy $E_{\mathrm{ind,resp}}^{(30)} \equiv J^{(3)}$ reads:

$$E_{\mathrm{ind,resp}}^{(30)} = \langle C_{\mathrm{A}}^{(1)}|[\Omega_{\mathrm{B}}, C_{\mathrm{A}}^{(1)}]\rangle_{\mathrm{A}} + \langle C_{\mathrm{B}}^{(1)}|[\Omega_{\mathrm{A}}, C_{\mathrm{B}}^{(1)}]\rangle_{\mathrm{B}} + 2\langle C_{\mathrm{A}}^{(1)}|VC_{\mathrm{B}}^{(1)}\rangle + 2\langle VC_{\mathrm{A}}^{(1)}C_{\mathrm{B}}^{(1)}\rangle + \langle C_{\mathrm{A}}^{(1)}|W_{\mathrm{A}}(C_{\mathrm{A}}^{(1)})^2\rangle_{\mathrm{A}} + \langle C_{\mathrm{B}}^{(1)}|W_{\mathrm{B}}(C_{\mathrm{B}}^{(1)})^2\rangle_{\mathrm{B}}. \tag{28}$$

When the orbitals are real, as we assume, the third and fourth terms in Eq. (28) are identical. We keep these terms separate since their physical origin is different and such terms are represented by entirely different diagrams.

The formula for $J^{(3)}$ should be compared to the one for the nonrelaxed third-order induction energy [36]:

$$E_{\mathrm{ind}}^{(30)} = \langle S_{\mathrm{A}}|[\Omega_{\mathrm{B}}, S_{\mathrm{A}}]\rangle_{\mathrm{A}} + \langle S_{\mathrm{B}}|[\Omega_{\mathrm{A}}, S_{\mathrm{B}}]\rangle_{\mathrm{B}} + 2\langle S_{\mathrm{A}}|VS_{\mathrm{B}}\rangle + 2\langle VS_{\mathrm{A}}S_{\mathrm{B}}\rangle, \tag{29}$$

expressed in terms of the induction operators (generating the first-order induction wave functions acting on Φ_{A} and Φ_{B}) $S_{\mathrm{A}} = s_{\rho}^{\alpha}a^{\rho}a_{\alpha}$ and $S_{\mathrm{B}} = s_{\sigma}^{\beta}b^{\sigma}b_{\beta}$, where s_{ρ}^{α} and s_{σ}^{β} are linear coefficients. S_{A} and S_{B} are the uncoupled counterparts of the CPHF operators $C_{\mathrm{A}}^{(1)}$ and $C_{\mathrm{B}}^{(1)}$. Specifically, the operator S_{A} is defined by Eq. (16) with H_{A} replaced by F_{A} and a similar definition holds for S_{B}. Thus, the formula for the relaxed third-order induction energy $E_{\mathrm{ind,resp}}^{(30)}$ is obtained from the one for $E_{\mathrm{ind}}^{(30)}$ when the uncoupled induction amplitudes s_{ρ}^{α} and s_{σ}^{β} are replaced by the coupled ones C_{ρ}^{α} and C_{σ}^{β} and two additional terms, the last two in Eq. (28), are added. The essential difference between $E_{\mathrm{ind}}^{(30)}$ and $E_{\mathrm{ind,resp}}^{(30)}$ (the same as between $E_{\mathrm{ind}}^{(20)}$ and $E_{\mathrm{ind,resp}}^{(20)}$) is that $E_{\mathrm{ind}}^{(30)}$ is strictly of the zeroth order in the intramonomer correlation operators W_{A} and W_{B}, while $E_{\mathrm{ind,resp}}^{(30)}$ includes terms of the first order [see the last two terms in Eq. (28)] as well as of higher order in W_{A} and W_{B} (via the CPHF operators $C_{\mathrm{A}}^{(1)}$ and $C_{\mathrm{B}}^{(1)}$). The correlation effect included in $E_{\mathrm{ind,resp}}^{(30)}$, resulting from the orbital relaxation, is sometimes referred to as the "apparent correlation" [26].

The formula expressing $E_{\mathrm{ind,resp}}^{(30)}$ in terms of molecular integrals and orbital energies can be derived from Eq. (28) using standard techniques of manipulating creation and annihilation operators. The second-quantized representations of the operators involved are [35, 42]

$$V = \tilde{v}_{\mu\nu}^{\lambda\kappa}a^{\mu}a_{\lambda}b^{\nu}b_{\kappa}, \tag{30}$$

$$W_{\mathrm{A}} = \frac{1}{4}w_{\mu\nu}^{\lambda\kappa}a^{\mu}a^{\nu}a_{\kappa}a_{\lambda} - w_{\nu\alpha}^{\mu\alpha}a^{\nu}a_{\mu}, \tag{31}$$

and similarly for W_{B}. The coefficients $w_{\mu\nu}^{\lambda\kappa}$ and $\tilde{v}_{\mu\nu}^{\lambda\kappa}$ are related to the two-electron integrals

$$v_{\mu\nu}^{\lambda\kappa} = \int\int \phi_{\mu}(\mathbf{r}_1)\phi_{\nu}(\mathbf{r}_2)\frac{1}{r_{12}}\phi_{\lambda}(\mathbf{r}_1)\phi_{\kappa}(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \tag{32}$$

by

$$w_{\mu\nu}^{\lambda\kappa} = v_{\mu\nu}^{\lambda\kappa} - v_{\mu\nu}^{\kappa\lambda}, \tag{33}$$

$$\tilde{v}_{\mu\nu}^{\lambda\kappa} = v_{\mu\nu}^{\lambda\kappa} + (v_{\mathrm{A}})_{\nu}^{\kappa} S_{\mu}^{\lambda}/N_{\mathrm{A}} + (v_{\mathrm{B}})_{\mu}^{\lambda} S_{\nu}^{\kappa}/N_{\mathrm{B}} + V_0 S_{\mu}^{\lambda} S_{\nu}^{\kappa}/N_{\mathrm{A}}N_{\mathrm{B}}, \tag{34}$$

where V_0 is the constant nuclear repulsion energy, $(v_{\mathrm{X}})_{\mu}^{\nu} = \langle\phi_{\mu}|v_{\mathrm{X}}\phi_{\nu}\rangle$ (X=A or B) is the matrix element of the attractive potential generated by the nuclei of monomer X, and $S_{\mu}^{\nu} = \langle\phi_{\mu}|\phi_{\nu}\rangle$ is an overlap integral. The (spin-free) CPHF coefficients C_r^a for monomer A fulfill the system of equations

$$\begin{aligned}(\epsilon_r - \epsilon_a)C_r^a &+ (2v_{ra'}^{ar'} - v_{ra'}^{r'a})C_{r'}^{a'} \\ &+ (2v_{rr'}^{aa'} - v_{rr'}^{a'a})C_{a'}^{r'} + (\omega_{\mathrm{B}})_r^a = 0,\end{aligned} \tag{35}$$

where $(\omega_{\mathrm{B}})_r^a = 2v_{rb}^{ab} + (v_{\mathrm{B}})_r^a$ is the matrix element of the complete electrostatic potential of the monomer B described by its HF determinant Φ_{B}, cf. Eq. (17), and ϵ_k is a monomer HF orbital energy. In Eq. (35), the indices a and r refer to occupied and virtual orbitals from monomer A. The corresponding orbitals from monomer B will be denoted by b and s.

Using the second-quantized representations of the operators V, W_{X}, and $C_{\mathrm{X}}^{(1)}$ (X=A or B) given earlier, one can prove that the third-order relaxed induction energy, Eq. (28), can be expressed as

$$\begin{aligned}E_{\mathrm{ind,resp}}^{(30)} = {} & 2C_a^r(\omega_{\mathrm{B}})_r^{r'}C_{r'}^a - 2C_a^r(\omega_{\mathrm{B}})_{a'}^{a}C_r^{a'} + 2C_b^s(\omega_{\mathrm{A}})_s^{s'}C_{s'}^b \\ & - 2C_b^s(\omega_{\mathrm{A}})_{b'}^{b}C_s^{b'} + 16v_{rs}^{ab}C_a^rC_b^s \\ & + 8C_a^r v_{a'r}^{r'r''}C_{r'}^{a'}C_{r''}^{a} - 4C_a^r v_{a'r}^{r''r'}C_{r'}^{a'}C_{r''}^{a} \\ & + 4C_a^r v_{a'a''}^{ar'}C_{r'}^{a'}C_r^{a''} - 8C_a^r v_{a'a''}^{r'a}C_{r'}^{a'}C_r^{a''} \\ & + 8C_b^s v_{b's}^{s's''}C_{s'}^{b'}C_{s''}^{b} - 4C_b^s v_{b's}^{s''s'}C_{s'}^{b'}C_{s''}^{b} \\ & + 4C_b^s v_{b'b''}^{bs'}C_{s'}^{b'}C_s^{b''} - 8C_b^s v_{b'b''}^{s'b}C_{s'}^{b'}C_s^{b''},\end{aligned} \tag{36}$$

where the matrix elements of the electrostatic potential generated by the HF-level monomer B are [36]

$$(\omega_{\mathrm{B}})_r^{r'} = 2\tilde{v}_{rb}^{r'b} - \frac{2}{N_{\mathrm{A}}}(v_{\mathrm{A}})_b^b\delta_r^{r'} - \frac{1}{N_{\mathrm{A}}}V_0\delta_r^{r'} = 2v_{rb}^{r'b} + (v_{\mathrm{B}})_r^{r'}, \tag{37}$$

$$(\omega_{\mathrm{B}})_a^{a'} = 2\tilde{v}_{ab}^{a'b} - \frac{2}{N_{\mathrm{A}}}(v_{\mathrm{A}})_b^b\delta_a^{a'} - \frac{1}{N_{\mathrm{A}}}V_0\delta_a^{a'} = 2v_{ab}^{a'b} + (v_{\mathrm{B}})_a^{a'}, \tag{38}$$

and similarly for monomer A. The sum of the first five terms on the r.h.s. of Eq. (36) is identical with the expression for the nonrelaxed induction energy $E_{\mathrm{ind}}^{(30)}$ [36], except that the CPHF coefficients C_r^a, C_s^b have taken the place of the (uncoupled) induction amplitudes s_r^a, s_s^b. The remaining terms in Eq. (36) arise from the additional W_{X}-dependent contributions given by the last two terms in Eq. (28). Once all relevant two-electron integrals in the molecular-orbital basis are known and the CPHF coefficients have been determined, the calculation of $E_{\mathrm{ind,resp}}^{(30)}$ is computationally only slightly more demanding than for $E_{\mathrm{ind}}^{(30)}$, but still very inexpensive compared to most other SAPT contributions (the scaling with respect to the numbers of occupied and virtual orbitals (o, v) for a monomer is ov^3 for $E_{\mathrm{ind,resp}}^{(30)}$ versus o^2v^2 for $E_{\mathrm{ind}}^{(30)}$).

At distances around the van der Waals minimum, the third-order induction energy is significantly (sometimes nearly completely [36]) quenched by its exchange counterpart. In fact, the large, mutually canceling terms arising in $E_{\mathrm{ind}}^{(30)}$ and $E_{\mathrm{exch-ind}}^{(30)}$ are a manifestation of the overall divergence of the polarization approximation [34, 43, 44], the basis of the SAPT approach. Thus, $E_{\mathrm{ind,resp}}^{(30)}$ should not be included in the SAPT interaction energy without its exchange counterpart. However, a derivation of the relaxed third-order exchange-induction energy $E_{\mathrm{exch-ind,resp}}^{(30)}$ is a rather nontrivial task and has not been achieved thus far. One should note that this correction, unlike $E_{\mathrm{ind,resp}}^{(30)}$, cannot be expressed through the first-order CPHF operators $C_{\mathrm{A}}^{(1)}$ and $C_{\mathrm{B}}^{(1)}$ alone. The operators $C_{\mathrm{A}}^{(2)}$ and $C_{\mathrm{B}}^{(2)}$ are also required since Wigner's $2n + 1$ rule does not hold when symmetry adaptation is applied. One may hope, just like it is usually assumed for second-order SAPT(DFT) exchange corrections [12, 13], that the inclusion of the orbital relaxation effects has a similar percentage effect on $E_{\mathrm{ind}}^{(30)}$ and on $E_{\mathrm{exch-ind}}^{(30)}$, i.e., that the relaxed third-order exchange-induction energy can be approximated by scaling the nonrelaxed third-order exchange-induction energy

$$\tilde{E}_{\mathrm{exch-ind,resp}}^{(30)} = E_{\mathrm{exch-ind}}^{(30)}\frac{E_{\mathrm{ind,resp}}^{(30)}}{E_{\mathrm{ind}}^{(30)}}. \tag{39}$$

We shall use this approximation in the calculations reported in the next Section.

3 Results and discussion

The orbital expression for the complete relaxed third-order induction energy, Eq. (36), has been implemented within the general-purpose closed-shell SAPT code [37]. This code, supplied with the atomic integrals and monomer HF orbitals computed by either ATMOL [45] or DALTON [46], has been used to obtain all the SAPT results presented here. To find out how the inclusion of $E_{\mathrm{ind,resp}}^{(30)}$ affects the conclusions about the importance of the third-order effects, reached in Ref. [36], we have performed calculations for all model dimers considered in Ref. [36], that is, for the He–He, He–LiH, Ar–Ar, H_2–CO, H_2O–H_2O, and H_2O–NH_3 systems, using exactly the same geometries (close to the equilibrium configurations) and basis sets as specified in Table 1 of Ref. [36]. The only exception is the helium dimer, for which we used only the aug-cc-pV6Z basis [47]

Table 1 Nonrelaxed and relaxed third-order SAPT corrections for several model dimers

Correction	He–He	He–LiH	Ar–Ar	H_2–CO	H_2O–H_2O	H_2O–NH_3
$\delta E_{\mathrm{int}}^{\mathrm{HF}}$	−0.4258	−22.0168	−5.4241	−12.9321	−286.2	−405.3
$E_{\mathrm{ind}}^{(30)}$	−0.1164	−40.4429	−188.7976	−13.8743	−826.1	−1264.4
$E_{\mathrm{ind,resp}}^{(30)}$	−0.1342	−60.3202	−229.2718	−17.6565	−1107.6	−1819.9
$E_{\mathrm{exch-ind}}^{(30)}$	0.0829	31.4352	188.5148	12.3362	745.0	1139.9
$\tilde{E}_{\mathrm{exch-ind,resp}}^{(30)}$	0.0956	46.8853	228.9284	15.6991	998.9	1640.7
$E_{\mathrm{ind}}^{(30)} + E_{\mathrm{exch-ind}}^{(30)}$	−0.0335	−9.0077	−0.2828	−1.5381	−81.1	−124.5
$E_{\mathrm{ind,resp}}^{(30)} + \tilde{E}_{\mathrm{exch-ind,resp}}^{(30)}$	−0.0386	−13.4348	−0.3434	−1.9574	−108.8	−179.2
$E_{\mathrm{ind-disp}}^{(30)}$	−0.1215	−9.9930	−13.6971	−6.4335	−194.6	−315.4
$E_{\mathrm{exch-ind-disp}}^{(30)}$	0.0749	5.6201	11.9681	4.3375	162.2	261.4
$E_{\mathrm{disp}}^{(30)}$	0.4003	1.3748	6.9402	7.1851	39.5	57.9
$E_{\mathrm{exch-disp}}^{(30)}$	−0.1176	−0.3856	−2.5713	−2.7526	−16.7	−24.9
$E_{\mathrm{int-corr}}^{(30)}$	0.2362	−3.3838	2.6399	2.3366	−9.6	−21.1
$E_{\mathrm{SAPT}}^{[2]}$	−10.8314	−142.7823	−104.9423	−97.5772	−1506.7	−1763.8
$E_{\mathrm{SAPT+HF}}^{[2]}$	−11.2572	−164.7990	−110.3665	−110.5092	−1792.8	−2169.0
$E_{\mathrm{SAPT}}^{[3]}$	−10.6287	−155.1737	−102.5852	−96.7787	−1597.4	−1909.4
$E_{\mathrm{SAPT+HF}}^{[3]}$	−11.0211	−168.1829	−107.7266	−108.1727	−1802.5	−2190.1
$E_{\mathrm{SAPT,resp}}^{[3]}$	−10.6339	−159.6009	−102.6459	−97.1980	−1625.1	−1964.1
CCSD(T)	−10.661	−177.162	−97.229	−90.026	−1731.7	−2079.7

The correction $\tilde{E}_{\mathrm{exch-ind,resp}}^{(30)}$ was obtained by scaling its nonrelaxed counterpart as described in the text. The (near-minimum) dimer geometries as well as the basis sets are specified in Table 1 of Ref. [36]. The energy unit is 1 K for He–He and 1 cm^{-1} for all the other systems

augmented by the $(6s6p6d3f1g1h)$ set of midbond functions, i.e., the largest of the basis sets employed in Ref. [36].

The third-order induction and exchange-induction corrections with and without relaxation (response), as well as all the parts of $E^{(30)}$ describing intermonomer correlation ($E_{\mathrm{ind-disp}}^{(30)}, E_{\mathrm{exch-ind-disp}}^{(30)}, E_{\mathrm{disp}}^{(30)}$, and $E_{\mathrm{exch-disp}}^{(30)}$), are presented in Table 1 for all six dimers listed earlier. These energies are compared to the values of $\delta E_{\mathrm{int}}^{\mathrm{HF}}$. The SAPT energies through second order in V, mostly at the standard level of theory, as well as several variants of the SAPT energy including effects of the third order in V are also presented and compared to the supermolecular counterpoise-corrected CCSD(T) energies calculated with the same basis set (using the MOLPRO code [48]). The notation for total SAPT energies follows that used in Ref. [36]. First, the SAPT energy through second order in V, without the $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ term, is defined as

$$E_{\mathrm{SAPT}}^{[2]} = E_{\mathrm{elst}}^{(1)} + E_{\mathrm{exch}}^{(1)} + E_{\mathrm{ind}}^{(2)} + E_{\mathrm{exch-ind}}^{(2)} + E_{\mathrm{disp}}^{(2)} + E_{\mathrm{exch-disp}}^{(2)}. \tag{40}$$

At the standard level of SAPT, the electrostatic energy $E_{\mathrm{elst}}^{(1)}$ is approximated through the third order in the intramonomer correlation operator $W = W_{\mathrm{A}} + W_{\mathrm{B}}$, i.e, by the expression $E_{\mathrm{elst}}^{(10)} + E_{\mathrm{elst,resp}}^{(12)} + E_{\mathrm{elst,resp}}^{(13)}$ [49] (the second superscript denotes the order in W). The first-order exchange energy is taken as $E_{\mathrm{exch}}^{(10)} + \epsilon_{\mathrm{exch}}^{(1)}(\mathrm{CCSD})$, where $\epsilon_{\mathrm{exch}}^{(1)}$ (CCSD) is the intramonomer correlation contribution to the first-order exchange energy approximately corresponding [50] to the coupled-cluster singles and doubles (CCSD) level of theory. The induction energy $E_{\mathrm{ind}}^{(2)}$ is approximated as $E_{\mathrm{ind,resp}}^{(20)} + {}^{t}E_{\mathrm{ind}}^{(22)}$, where ${}^{t}E_{\mathrm{ind}}^{(22)}$ is the "true" correlation part of $E_{\mathrm{ind}}^{(22)}$. In this way, the second-order (in W) "apparent" correlation effects included in $E_{\mathrm{ind,resp}}^{(20)}$ are not counted twice [50, 51]. In a similar way, the exchange-induction energy $E_{\mathrm{exch-ind}}^{(2)}$ is interpreted as $E_{\mathrm{exch-ind,resp}}^{(20)} + {}^{t}E_{\mathrm{exch-ind}}^{(22)}$, where ${}^{t}E_{\mathrm{exch-ind}}^{(22)}$ is approximated by an appropriate scaling of ${}^{t}E_{\mathrm{ind}}^{(22)}$ [1, 51]. The dispersion energy $E_{\mathrm{disp}}^{(2)}$ is approximated through second order in W as $E_{\mathrm{disp}}^{(20)} + E_{\mathrm{disp}}^{(21)} + E_{\mathrm{disp}}^{(22)}$ [35] and the small exchange-dispersion contribution $E_{\mathrm{exch-disp}}^{(2)}$ is approximated by $E_{\mathrm{exch-disp}}^{(20)}$ [35]. A more detailed description of the algorithms used to compute the SAPT corrections listed here can be found in Refs. [41] and [52].

Similarly as in Ref. [36], for the He_2 and He–LiH dimers we were able to go beyond the standard level and use a somewhat better approximation to $E^{(2)}_{\rm disp}$, denoted by $E^{(2)}_{\rm disp}$ [CCD+ST(CCD)], resulting from an infinite-order (in W) summation [53] of coupled-cluster diagrams contributing to $E^{(2)}_{\rm disp}$. For the He_2 dimer only, we evaluated $E^{(1)}_{\rm elst}+E^{(1)}_{\rm exch}$ exactly (for a given basis) by using the configuration functions for monomers [54].

The quantity $E^{[2]}_{\rm SAPT+HF}$ and all variants of $E^{[3]}$ can be defined as follows,

$$E^{[2]}_{\rm SAPT+HF} = E^{[2]}_{\rm SAPT} + \delta E^{\rm HF}_{\rm int}, \tag{41}$$

$$E^{[3]}_{\rm SAPT} = E^{[2]}_{\rm SAPT} + E^{(30)}_{\rm ind} + E^{(30)}_{\rm exch-ind} + E^{(30)}_{\rm int-corr}, \tag{42}$$

$$E^{[3]}_{\rm SAPT+HF} = E^{[2]}_{\rm SAPT+HF} + E^{(30)}_{\rm int-corr}, \tag{43}$$

$$E^{[3]}_{\rm SAPT,resp} = E^{[2]}_{\rm SAPT} + E^{(30)}_{\rm ind,resp} + \tilde{E}^{(30)}_{\rm exch-ind,resp} + E^{(30)}_{\rm int-corr}, \tag{44}$$

where

$$E^{(30)}_{\rm int-corr} = E^{(30)}_{\rm ind-disp} + E^{(30)}_{\rm exch-ind-disp} + E^{(30)}_{\rm disp} + E^{(30)}_{\rm exch-disp} \tag{45}$$

is the *intermonomer* correlation part of the third-order SAPT energy $E^{(30)}_{\rm int}$ obtained with a complete neglect of intramonomer correlation. Note that at the second-order level the orbital relaxation is always included in all quantities.

The data collected in Table 1 show that the relaxed correction $E^{(30)}_{\rm ind,resp}$ is consistently larger in magnitude (more negative) than its nonrelaxed counterpart $E^{(30)}_{\rm ind}$, the ratio of these two energies varying between 1.15 and 1.5 for the 6 systems considered. As the approximation (39) implies, $\tilde{E}^{(30)}_{\rm exch-ind,resp}$ is also larger than $E^{(30)}_{\rm exch-ind}$, and the sum $E^{(30)}_{\rm ind,resp}+\tilde{E}^{(30)}_{\rm exch-ind,resp}$ is more negative than $E^{(30)}_{\rm ind}+E^{(30)}_{\rm exch-ind}$. However, the $\delta E^{\rm HF}_{\rm int}$ correction is still significantly more negative. Thus, while the inclusion of the orbital relaxation effects improves the agreement between $\delta E^{\rm HF}_{\rm int}$ and its third-order SAPT approximation, this improvement is relatively small at the near-equilibrium geometries.

It is interesting to note that the $E^{(30)}_{\rm ind,resp}$ energy is strongly dominated by the first five terms in Eq. (36) (or, equivalently, by the first four terms in Eq. (28)). The additional W_A and W_B-dependent terms, which do not appear in the nonrelaxed correction $E^{(30)}_{\rm ind}$, contribute no more than 2% of the value of $E^{(30)}_{\rm ind,resp}$ and are positive for all systems considered. These terms become somewhat more important, however, at larger intermonomer separations and are needed to accurately reproduce the large-R asymptotic behavior of $\delta E^{\rm HF}_{\rm int}$.

Based on the results including the nonrelaxed corrections $E^{(30)}_{\rm ind}$ and $E^{(30)}_{\rm exch-ind}$ only, we previously recommended [36] to choose as the final SAPT interaction energy the quantity $E^{[3]}_{\rm SAPT+HF}$ (including $\delta E^{\rm HF}_{\rm int}$) if monomers are polar (and thus induction effects are strong) and $E^{[3]}_{\rm SAPT}$ (including $E^{(30)}_{\rm ind}+E^{(30)}_{\rm exch-ind}$ instead) if monomers are nonpolar or weakly polar. For the systems in Table 1, this corresponds to taking $E^{[3]}_{\rm SAPT+HF}$ for He–LiH, H_2O–H_2O, and H_2O–NH_3, and $E^{[3]}_{\rm SAPT}$ for He–He, Ar–Ar, and H_2–CO. As the results in Table 1 indicate, while the inclusion of relaxation effects does somewhat improve the agreement between $E^{[3]}_{\rm SAPT,resp}$ and the CCSD(T) interaction energies (compared to that in the case of using $E^{[3]}_{\rm SAPT}$) for polar monomers and worsens this agreement only insignificantly for nonpolar ones, the general recommendations of Ref. [36] do not change. For the former type of monomers, contrary to the conjecture of Ref. [36], the energy $E^{[3]}_{\rm SAPT,resp}$ is further from the CCSD(T) interaction energy than $E^{[3]}_{\rm SAPT+HF}$, so that the calculation of the $\delta E^{\rm HF}_{\rm int}$ term cannot be avoided for such systems. Even though this conclusion is based on approximate, scaled values $\tilde{E}^{(30)}_{\rm exch-ind,resp}$, Eq. (39), it is highly unlikely that it would have changed had the exact results been available. A similar scaling approximation works very well for the relaxed second-order exchange-induction energy. In fact, the ratio $(E^{(20)}_{\rm exch-ind,resp}/E^{(20)}_{\rm ind,resp})/(E^{(20)}_{\rm exch-ind}/E^{(20)}_{\rm ind})$ is very close to one (in the range 0.98–1.06) for all systems in Table 1. The success of the scaling approximation in the second order is clearly related to the fact that both $E^{(20)}_{\rm ind,resp}$ and $E^{(20)}_{\rm exch-ind,resp}$ are linear in the CPHF coefficients C^a_r and C^b_s [41]. Although in the third order the dependence on the CPHF coefficients is more complicated, $E^{(30)}_{\rm ind,resp}$ is strongly dominated by a contribution (the first two lines of Eq. (36)) that is quadratic in C^a_r, C^b_s. If a similar situation exists for $E^{(30)}_{\rm exch-ind,resp}$, which is likely the case, the scaling approximation (39) can be expected to work just as well as in the second order.

For the helium dimer, the energies in Table 1 can also be compared with the full configuration interaction (FCI) result in the same basis set, equal to -10.983 K (Ref. [36]). Such a comparison shows that the CCSD(T) and third-order SAPT results differ from the FCI one by about the same amount. The $E^{[3]}_{\rm SAPT+HF}$ result is very close to FCI, but in view of the other evidence we have to conclude that this agreement is fortuitous.

As shown in Table 1, while the inclusion of the response effects in the third order (in an exact way for $E^{(30)}_{\rm ind}$ and an approximate way for $E^{(30)}_{\rm exch-ind}$) does improve the agreement

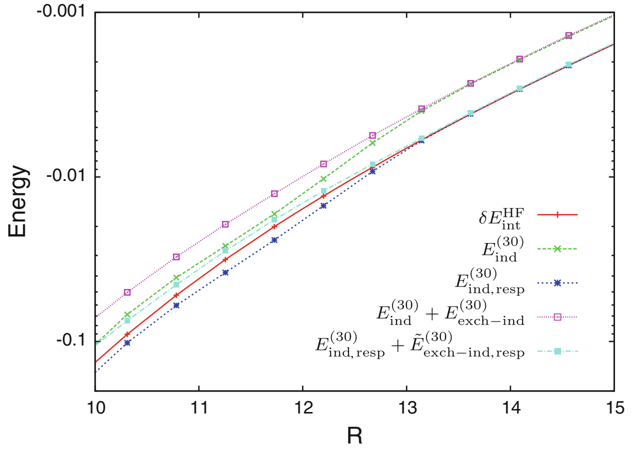

Fig. 1 Nonrelaxed and relaxed third-order induction and exchange-induction energies (in cm^{-1}) versus the $\delta E^{\rm HF}_{\rm int}$ term for the water dimer at asymptotic separations, as functions of the intermolecular center-of-mass distance R (in bohr). The angular orientation of monomers is kept the same as for the near-minimum geometry in Table 1 (specified in Table 1 of Ref. [36])

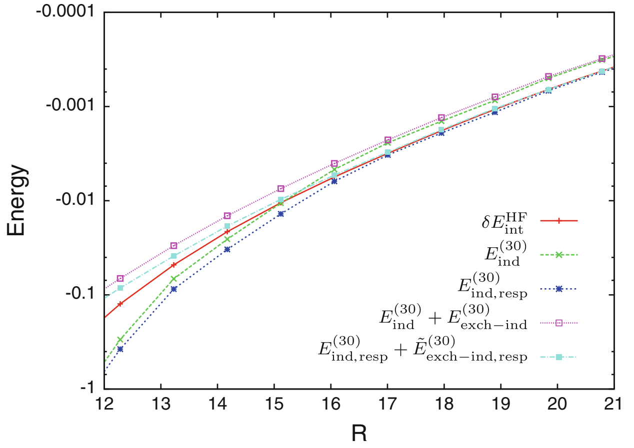

Fig. 2 Nonrelaxed and relaxed third-order induction and exchange-induction energies (in cm^{-1}) versus the $\delta E^{\rm HF}_{\rm int}$ term for the NH$_3$–ClF dimer at asymptotic separations, as functions of the intermolecular-center-of-mass distance R (in bohr). The angular orientation of monomers is kept the same as in the CT7/04 database [55]

between $\delta E^{\rm HF}_{\rm int}$ and its SAPT approximation, this improvement is relatively minor for intermonomer separations corresponding to van der Waals minima. On the other hand, for larger separations the sum $E^{(30)}_{\rm ind,resp} + \tilde{E}^{(30)}_{\rm exch-ind,resp}$ is clearly superior to $E^{(30)}_{\rm ind} + E^{(30)}_{\rm exch-ind}$ since only the former one recovers the leading-order asymptotics of $\delta E^{\rm HF}_{\rm int}$. This behavior is illustrated in Figs. 1 and 2, where we plotted $E^{(30)}_{\rm ind}$ and $E^{(30)}_{\rm ind,resp}$, with or without their exchange counterparts, as well as the $\delta E^{\rm HF}_{\rm int}$ term, as functions of the center-of-mass distance R for the H$_2$O–H$_2$O (Fig. 1) and NH$_3$–ClF (Fig. 2) dimers. The NH$_3$–ClF dimer, with the monomer geometry and orientation taken from the CT7/04 database [55], was chosen because it has been found to have particularly large induction and exchange-induction energies in the SAPT(DFT) study performed in Ref. [56]. For this system, we employed the aug-cc-pVTZ basis plus a (3*s*3*p*2*d*2*f*) set of midbond functions, i.e., the same basis as in Ref. [56]. For the water dimer, the angular orientation of the monomers was the same as for the near-minimum geometry (Table 1). Figures 1 and 2 clearly show that at distances where the overlap of monomer charge densities is minimal as indicated by the vanishing of $E^{(30)}_{\rm exch-ind}$ and $\tilde{E}^{(30)}_{\rm exch-ind,resp}$, it is the relaxed third-order induction energy that fully agrees with the supermolecular $\delta E^{\rm HF}_{\rm int}$ term. The nonrelaxed correction $E^{(30)}_{\rm ind}$ does capture the $-C_9/R^9$ decay of $\delta E^{\rm HF}_{\rm int}$, as indicated by the respective curves being parallel on the logarithmic scale. However, the C_9 constant is wrong unless the response effects are included. A similar situation arises in the second order in V where the correction $E^{(20)}_{\rm ind,resp}$, unlike its nonrelaxed counterpart, recovers exactly the leading $-C_6/R^6$ term in the asymptotic decay of $E^{\rm HF}_{\rm int} - E^{(10)}_{\rm elst} - E^{(10)}_{\rm exch}$.

4 Summary and conclusions

We have presented an extension of the symmetry-adapted perturbation theory by including the orbital relaxation effects in the treatment of the third-order induction interaction. This development complements that of Ref. [36], where the nonrelaxed third-order induction energy together with the corresponding exchange damping was given. In the present work, the exchange damping of the relaxed induction energy was included by properly scaling the third-order exchange-induction correction developed in Ref. [36]. The inclusion of the exchange damping of the relaxed third-order induction energy is shown to be indispensable because of the strong cancelation of the induction and exchange-induction effects at short intermonomer separations. The numerical results for a series of model dimers representing various strengths and types of interaction show that the relaxation effect substantially increases the third-order induction interaction. This increase varies from 15% for the dispersion-dominated He$_2$ dimer to 50% for the induction-bound He–LiH complex. At large intermonomer separations, the relaxed third-order induction energy perfectly recovers the $\delta E^{\rm HF}_{\rm int}$ correction often used in SAPT to estimate the effects of the third- and higher-order contributions in V. This agreement confirms the correctness of our theoretical formulation and of the codes used in our calculations.

At the near-equilibrium geometries, we have found that $\delta E^{\rm HF}_{\rm int}$ and the sum $E^{(30)}_{\rm ind,resp} + \tilde{E}^{(30)}_{\rm exch-ind,resp}$ differ quite significantly. For nonpolar systems, this difference is particularly large as a fraction of $\delta E^{\rm HF}_{\rm int}$ and at the same time the sum of third-order corrections is small in magnitude. Therefore, this difference is expected to be due to unphysical components of the Hartree–Fock interaction energy. For the polar systems, the difference is much smaller. It is probably due mainly to contributions beyond the third order.

We have also compared the complete correlated SAPT calculations through second and third order with the CCSD(T) interaction energies computed in the same basis sets. This comparison corroborates the observation made in Ref. [36] that for nonpolar, dispersion-bound systems, the pure SAPT through third order is more accurate than the hybrid treatment employing the $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ correction. This behavior is consistent with the assumption that the $\delta E_{\mathrm{int}}^{\mathrm{HF}}$ correction includes nonphysical, short-range terms, which become visible for nonpolar systems.

For the polar systems considered by us, the hybrid SAPT approach remains more accurate near the minima although the inclusion of the third-order relaxation effects appreciably improves the performance of pure SAPT and makes it more competitive with the hybrid approach. The same inclusion makes the pure and hybrid SAPT energies agree even better as the intermonomer separation increases, as the leading-order asymptotic behavior of $E_{\mathrm{ind,resp}}^{(30)}$, unlike for $E_{\mathrm{ind}}^{(30)}$, is the same as of $\delta E_{\mathrm{int}}^{\mathrm{HF}}$. It is hard to say at the moment what the origin of the remaining discrepancy between pure SAPT and CCSD(T) calculations is. Besides residual intramonomer correlation effects of the first and second order in V, this could be intramonomer correlation effects of the third order in V or possibly the leading fourth- and even higher-order effects. Finally, the effects of the excitations neglected in the CCSD(T) approach might be just as important at this level of accuracy, as we have observed for the helium dimer where a comparison with the FCI benchmark is possible.

Acknowledgments This work was supported by the NSF grant CHE-0848589.

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