Second-order exchange-induction energy of intermolecular interactions from coupled cluster density matrices and their cumulants

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A new formulation of the second-order exchange-induction energy of symmetry-adapted perturbation theory is presented. In the proposed formalism the exchange-induction energy is expressed through one- and two-particle reduced density matrices of monomers, which are of zeroth and first order with respect to the effective electrostatic potential of another monomer. The resulting expression is further modified by using the partition of two-particle density matrices into the antisymmetrized product of one-particle density matrices and the remaining cumulant part. The proposed formalism has been applied to the case of closed-shell monomers and for density matrices obtained from the expectation-value expression with coupled cluster singles and doubles wave functions. The performance of the new approach has been demonstrated on several benchmark van der Waals systems, including dimers of argon, water, and ethyne.

I. Introduction

Symmetry-adapted perturbation theory (SAPT) (see ref. 1–3 for reviews and ref. 4–10 for example applications) has become a well established method for calculations of the interaction energy between two closed-shell molecules. In SAPT the Hamiltonian H of a dimer AB is divided into the unperturbed part, being the sum of the monomer Hamiltonians, H_A and H_B, and the interaction operator V. If Rayleigh-Schrödinger perturbation theory (RSPT) is applied to such a partition of the Hamiltonian (in this case RSPT is often called a *polarization theory*[11]), then up to the second order in V the following contributions to the interaction energy are obtained: first-order electrostatics ($E_{\text{elst}}^{(1)}$), second-order induction ($E_{\text{ind}}^{(2)}$) and second-order dispersion ($E_{\text{disp}}^{(2)}$) energies. Since the zeroth-order wave function in polarization theory is not antisymmetric with respect to the electron exchange between monomers, this approach is incapable of accounting for the electron exchange effects for medium and large distances between monomers (at least in a finite order, see ref. 12 and 13), Jeziorski and Kołos[12] proposed to apply operators that force a proper permutational symmetry of approximate wave functions. Further investigations of symmetry-forcing methods (see ref. 1 for a review) lead to the conclusion that one of the simplest approaches, called *symmetrized* RS (SRS) theory,[14] gives the interaction energy that in the second order compares favorably with the exact energy for small test systems. In SRS, like in other symmetry-forcing schemes, each polarization correction is damped by its exchange counterpart, *i.e.* for the three low-order energy corrections listed above one has the following additional contributions: first-order exchange ($E_{\text{exch}}^{(1)}$), second-order exchange-induction ($E_{\text{exch-ind}}^{(2)}$) and second-order exchange-dispersion ($E_{\text{exch-disp}}^{(2)}$) energies. One can also say qualitatively that exchange corrections result from the

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overlap of monomers' electron clouds in the van der Waals region.

In practice, the exact solutions for monomer Schrödinger equations are not known, and one has to start from some approximate monomer wave functions instead. If the Hartree–Fock (HF) determinants are used for this purpose, then the so-called triple perturbation theory results.[15] In this approach the SAPT corrections to the interaction energy are expanded in terms of intramonomer fluctuation operators W_A and W_B (a fluctuation operator is a difference between the Hamiltonian and the Fock operator) *i.e.* two Møller–Plesset (MP) expansions are applied to each SAPT correction,[15]

$$E^{(n)} = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} E^{(nij)}. \tag{1}$$

[Here i and j are orders of a correction in terms of the fluctuation operators W_A and W_B, respectively.] Often a shorthand notation $E^{(nk)} = \sum_{l=0}^{k} E^{(nl(k-l))}$ is used to describe a correction of the cumulative (W_A or W_B) order equal to k.

The second-order exchange-induction energy can be obtained so far on the HF level.[16] Two versions of this correction are available, one corresponding to the uncoupled HF (UCHF),[17] and one to the coupled HF (CHF)[18,19] approach. For the latter case orbitals of the monomer are allowed to respond to the perturbing field of another monomer, so this correction is usually denoted as $E_{\text{exch-ind,resp}}^{(20)}$. It has been proved[20,21] that the $E_{\text{ind,resp}}^{(20)}$ and $E_{\text{exch-ind, resp}}^{(20)}$ energies are fully included into the supermolecular Hartree–Fock interaction energy, and should therefore be preferred over the UCHF corrections. Also, numerical experience shows that better results are usually obtained if the CHF exchange-induction energy is used.

On the other hand, the polarization counterpart of the $E_{\text{exch-ind}}^{(2)}$ correction, *i.e.* the second-order induction energy, is routinely calculated on the correlated MP2 level,[2,22]

$$E_{\text{ind}}^{(2)} \approx E_{\text{ind,resp}}^{(20)} + {}^{t}E_{\text{ind}}^{(22)}. \tag{2}$$

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Here the $^tE_{ind}^{(22)}$ term is a *true* correlation part of the $E_{ind}^{(22)}$ correction, *i.e.* the part *not* included into the $E_{ind,resp}^{(20)}$ energy.[2,22] One should note that $E_{ind,resp}^{(22)}$ was also derived and examined some time ago,[22] although it is not available in the SAPT system of codes.[16] Actually, this correction can be easily obtained from any *ab initio* program which is able to calculate analytically second-order static properties on the HF and MP2 levels (see, *e.g.* ref. 23).

It is known that the MP2 correlation contribution of the second-order induction energy can be responsible for a significant part of the total interaction energy (*e.g.* 7% for the water dimer in the minimum region[24]). On the other hand, numerous SAPT applications show that the second-order CHF induction energy is often damped substantially by its exchange counterpart, especially in the repulsive and minimum regions of the potential energy surface. Since the correlation part of the induction energy is not balanced by the corresponding exchange-induction term and the correlation contribution to the induction energy is usually negative, the interaction energies obtained by the SAPT approach tend to be too low. As a temporary fix to this problem a simple proportionality formula was proposed[16] which estimates the correlated part of the exchange-induction correction from the following expression,

$$^tE_{exch\text{-}ind}^{(22),estim.} = \frac{E_{exch\text{-}ind,resp}^{(20)}}{E_{ind,resp}^{(20)}} {}^tE_{ind}^{(22)}. \quad (3)$$

It is obvious that such an equation is not a satisfactory, physically-grounded solution of the problem and that the correlation contribution to the second-order exchange-induction energy should be treated with more care.

In this paper a density-matrix formulation of the second-order exchange-induction energy is proposed. The new approach makes it possible to derive this correction on any (correlated or not) level. As an example, the exchange-induction energy with monomers described by the coupled cluster singles and doubles (CCSD) wave functions has been implemented. The rest of this paper is organized as follows. In section II it will be shown how to express the exchange-induction energy in terms of one- and two-particle density matrices, which are of zeroth and first order with respect to the effective electrostatic potential of another monomer. The general orbital formulae will be presented in section III, while derivations specific to the coupled cluster (CC) implementation will be given in section IV. Finally, the results for several van der Waals complexes will be shown and discussed in section V, while the conclusions will be presented in section VI.

II. Theory

We consider the interaction of two closed-shell molecules A and B. The exact normalized wave function and the exact energy of the molecule X, $X = A, B$, are denoted by Ψ_X and E_X, respectively. The intermolecular potential V can be re-written for convenience in terms of a modified interelectron interaction potential $v(i,j)$,[1]

$$V = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} v(i,j),$$

$$v(i,j) = \frac{1}{r_{ij}} + \frac{1}{N_B} v_B(i) + \frac{1}{N_A} v_A(j)$$
$$+ \frac{1}{N_A N_B} \sum_{\alpha \in A} \sum_{\beta \in B} Z_\alpha Z_\beta \frac{1}{R_{\alpha\beta}}, \quad (4)$$

where i and j denote the coordinates of electrons belonging to the monomers A and B, respectively, N_A and N_B stand for the number of electrons in the monomers, and finally v_A and v_B are the electrostatic potentials of all nuclei in the respective monomers.

It is known that if a distance between closed-shell monomers is not too small, the multiple exchanges of electrons between monomers can be neglected.[25,26] The accuracy of this approximation (called the S^2 approximation) was verified for several small molecules.[25–27] Since only the exchange energies within the S^2 approximation will be considered here, the abbreviation S^2 will be omitted in this paper. The exchange-induction energy in the S^2 approximation is given by the following expression,[17]

$$E_{exch\text{-}ind}^{(2)} = \langle \Psi_A \Psi_B | (V - \bar{V})(P - \bar{P})(\Psi_A^{(1)}\Psi_B + \Psi_A\Psi_B^{(1)}) \rangle. \quad (5)$$

P in eqn (5) is a single-exchange operator (with an appropriate sign factor),

$$P = - \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} P_{ij}, \quad (6)$$

and $\bar{X}$ denotes an average value of the operator X with the wave function $\Psi_A\Psi_B$ (note that $\bar{V} = E_{elst}^{(1)}$). The first-order perturbed wave function $\Psi_A^{(1)}$ accounts for a modification of the wave function of the monomer A caused by the effective electrostatic field $V_{eff,B}$ of the monomer B, that is defined as,

$$V_{eff,B} = \sum_{i=1}^{N_A} \left(v_B(i) + \int \frac{1}{r_{ij}} \rho_B(j) d\tau_j \right). \quad (7)$$

where $\rho_B(j)$ is the one-particle density of the monomer B. The function $\Psi_A^{(1)}$ can be found from the textbook formula

$$\Psi_A^{(1)} = -R_0^A V_{eff,B} \Psi_A, \quad (8)$$

where R_0^A is the reduced resolvent of the monomer A (note that the perturbed wave function is orthogonal to the unperturbed one: $\langle \Psi_A^{(1)} | \Psi_A \rangle = 0$). The formulae for the wave function $\Psi_B^{(1)}$ can be obtained from eqns (7) and (8) by interchanging indices A and B.

Let us consider the first part of the exchange-induction energy from eqn (5), resulting from perturbing of monomer A by monomer B,

$$E_{exch\text{-}ind}^{(2)} (A \leftarrow B) = \langle \Psi_A \Psi_B | (V - \bar{V})(P - \bar{P})\Psi_A^{(1)}\Psi_B \rangle \quad (9)$$

Our goal is to express eqn (9) in terms of monomers' reduced density matrices.[28] To this end the method analogous to the approach presented by Moszynski *et al.*[29] will be used here. After inserting into eqn (9) the expressions for the interaction potential V (eqn (4)) and the single-exchange operator P

(eqn (6)) and performing some algebraic manipulations, the following final formula is obtained for the correction $E_{\text{exch-ind}}^{(2)}$ $(A \leftarrow B)$,

$$E_{\text{exch-ind}}^{(2)}(A \leftarrow B) = \int (\rho_{\text{int},A}^{(1)}(1|1') - \bar{P}\rho_{A\leftarrow B}^{(1)}(1|1)\rho_B(1'|1'))$$
$$\times \left(v(1,1') - \frac{\bar{V}}{N_A N_B} \right) d\tau_1 d\tau_1'.$$
$$(10)$$

In eqn (10) $\rho_{\text{int},A}^{(1)}(1|1')$ denotes the first-order interaction density matrix defined as,

$$\rho_{\text{int},A}^{(1)}(1|1') = -\rho_{A\leftarrow B}^{(1)}(1|1')\rho_B(1'|1)$$
$$- \int \rho_{A\leftarrow B}^{(1)}(1|2')\Gamma_B(1'2'|1'1)d\tau_2$$
$$- \int \Gamma_{A\leftarrow B}^{(1)}(12|11')\rho_B(1'|2)d\tau_2$$
$$- \int \Gamma_{A\leftarrow B}^{(1)}(12|12')\Gamma_B(1'2'|1'2)d\tau_2 d\tau_2'.$$
$$(11)$$

In eqn (11) first-order one- and two-particle reduced density matrices of the monomer A perturbed by the effective potential $V_{\text{eff},B}$ were introduced,

$$\rho_{A\leftarrow B}^{(1)}(1|1') = N_A \int \Psi^*_A(1,2,\ldots,N_A)\Psi_A^{(1)}(1',2,\ldots,N_A)d\tau_2\ldots\tau_{N_A},$$
$$\Gamma_{A\leftarrow B}^{(1)}(12|1'2') = N_A(N_A - 1) \int \Psi^*_A(1,2,\ldots,N_A)$$
$$\times \Psi_A^{(1)}(1',2',3,\ldots,N_A)d\tau_3\ldots\tau_{N_A}, \quad (12)$$

Let us remember that the ground-state reduced density matrices of the monomer B are defined as,

$$\rho_B(1|1') = N_B \int \Psi^*_B(1,2,\ldots,N_B)\Psi_B(1',2,\ldots,N_B)d\tau_2\ldots\tau_{N_B},$$
$$\Gamma_B(12|1'2') = N_B(N_B - 1) \int \Psi^*_B(1,2,\ldots,N_B)$$
$$\times \Psi_B(1',2',3,\ldots,N_B)d\tau_3\ldots\tau_{N_B}. \quad (13)$$

The quantities from eqn (13) will be often referenced as zeroth-order in this paper, which means that they are independent of the perturbation $V_{\text{eff},B}$. The first-order interaction density matrix $\rho_{\text{int},B}^{(1)}(1|1')$ can be obtained from eqn (11) by interchanging indices A and B. Formula (10) for the second-order exchange-induction energy has a very similar form to the expression for the first-order exchange energy in the S^2 approximation, presented by Moszynski et al.[29] In fact, the (zeroth-order) interaction density matrix introduced in ref. 29 can be retrieved from eqn (11) if all first-order density matrices are replaced by the zeroth-order ones. Similar quantities have been recently used in a derivation of third order SAPT corrections.[30]

Note that the induction energy $E_{\text{ind}}^{(2)}$ $(A \leftarrow B)$ can be described in terms of one-particle zeroth- and first-order densities as follows,

$$E_{\text{ind}}^{(2)}(A \leftarrow B) = \int \rho_{A\leftarrow B}^{(1)}(1|1)\rho_B(1'|1')v(1,1')d\tau_1 d\tau_1'. \quad (14)$$

The expression for the first-order interaction density matrix (eqn (11)) can be used to obtain consecutive terms of the MP series for the exchange-induction energy ($E_{\text{exch-ind}}^{(2k)}$) by expanding the density matrices and the effective potential $V_{\text{eff},B}$ in orders of the W_A and W_B operators and by gathering terms of the same order. Then the elimination of disconnected terms from eqn (10) should be performed in each MP order

separately. A similar procedure has been used by Moszynski et al. to derive electrostatic and first-order exchange corrections.[29,31] For the case of the first-order exchange energy it was then realized[29] that the convergence of the resulting MP series ($E_{\text{exch}}^{(1k)}$) is only moderately fast. As a solution to this problem Moszynski et al.[29] proposed to replace MP1 and MP2 amplitudes of monomers by their converged CCSD amplitudes in the equations for the intramonomer correlation corrections to the first-order exchange energy. Anticipating similar problems for the exchange-induction energy, it has been decided here to concentrate from the beginning on the nonperturbative treatment of the intramonomer correlation.

The elimination of disconnected terms can be simplified if the cumulant approach, introduced in quantum chemistry by Kutzelnigg and Mukherjee[32–34] and Mazziotti,[35,36] is applied to the two-particle density matrices. Cumulants have recently been used to obtain the first-order exchange energy on the coupled cluster singles and doubles level.[37] A cumulant Λ of a two-particle reduced density matrix Γ is defined as a difference between Γ and the density matrix which one could expect for independent fermions described by a one-particle density matrix ρ. Note that cumulants possess an important property of being size-extensive,[32] which makes them potentially useful tools in quantum chemistry. It follows from a definition of the cumulant Λ that one can express the density matrix Γ as[32]

$$\Gamma(12|1'2') = \rho(1|1')\rho(2|2') - \rho(1|2')\rho(2|1')$$
$$+ \Lambda(12|1'2'). \quad (15)$$

In the present paper it is proposed to use the following partition of the first-order two-particle density matrices, analogous to eqn (15),

$$\Gamma^{(1)}(12|1'2') = \rho^{(1)}(1|1')\rho(2|2') - \rho^{(1)}(1|2')\rho(2|1')$$
$$+ \rho(1|1')\rho^{(1)}(2|2') - \rho(1|2')\rho^{(1)}(2|1')$$
$$+ \Lambda^{(1)}(12|1'2'). \quad (16)$$

It should be stressed that if partitions from eqns (15) and (16) are used for approximate density matrices, it should always be verified whether a given method allows for a description in terms of cumulants, i.e. if a difference between the approximate two-particle density matrix and the antisymmetrized product of one-particle density matrices is a connected quantity.

The formula for the $E_{\text{exch-ind}}^{(2)}$ $(A \leftarrow B)$ energy (see eqn (10)) contains two explicitly disconnected parts. However, one can show by inserting eqns (15) and (16) into eqn (10) that these terms are cancelled by the disconnected elements resulting from the noncumulant part of the two-particle density matrices, and that the final formula for the $E_{\text{exch-ind}}^{(2)}$ $(A \leftarrow B)$ energy is composed by the connected terms only,

$$E_{\text{exch-ind}}^{(2)}(A \leftarrow B) = -(\mathcal{X}^{1A} + \mathcal{X}_n^{2A} + \mathcal{X}_n^{3A} + \mathcal{X}_n^{4A} + \mathcal{X}_c^{2A}$$
$$+ \mathcal{X}_c^{3A} + \mathcal{X}_{nc}^{4A} + \mathcal{X}_{cn}^{4A} + \mathcal{X}_{cc}^{4A}). \quad (17)$$

The capital letter A in the subscripts of the r.h.s. of eqn (17) denotes the perturbed monomer (in this case: the monomer A).

The nine elements of eqn (17) are defined as follows,

$$\mathscr{X}^{1A} = \int \rho_A^{(1)}(1|1')\rho_B(1'|1)v(1,1')d\tau_1 d\tau_1',$$

$$\mathscr{X}_n^{2A} = \int \rho_A^{(1)}(1|2')(\rho_B(1'|1')\rho_B(2'|1) - \rho_B(1'|1)\rho_B(2'|1'))v(1,1')d\tau_1 d\tau_1' d\tau_2',$$

$$\mathscr{X}_n^{3A} = \int(\rho_A^{(1)}(1|1)\rho_A(2|1') - \rho_A^{(1)}(1|1')\rho_A(2|1) + \rho_A(1|1)\rho_A^{(1)}(2|1') - \rho_A(1|1')\rho_A^{(1)}(2|1)) \times \rho_B(1'|2)v(1,1')d\tau_1 d\tau_1' d\tau_2,$$

$$\mathscr{X}_n^{4A} = \int(\rho_A^{(1)}(1|2')\rho_A(2|1)\rho_B(1'|2)\rho_B(2'|1') - \rho_A^{(1)}(1|1)\rho_A(2|2')\rho_B(1'|2)\rho_B(2'|1') - \rho_A^{(1)}(1|2')\rho_A(2|1)\rho_B(1'|1')\rho_B(2'|2) + \rho_A(1|2')\rho_A^{(1)}(2|1)\rho_B(1'|2)\rho_B(2'|1') - \rho_A(1|1)\rho_A^{(1)}(2|2')\rho_B(1'|2)\rho_B(2'|1') - \rho_A(1|2')\rho_A^{(1)}(2|1)\rho_B(1'|1')\rho_B(2'|2)) \times v(1,1')d\tau_1 d\tau_1' d\tau_2 d\tau_2',$$

$$\mathscr{X}_c^{2A} = \int \rho_A^{(1)}(1|2')\Lambda_B(1'2'|1'1)v(1,1')d\tau_1 d\tau_1' d\tau_2',$$

$$\mathscr{X}_c^{3A} = \int \Lambda_A^{(1)}(12|11')\rho_B(1'|2)v(1,1')d\tau_1 d\tau_1' d\tau_2,$$

$$\mathscr{X}_{nc}^{4A} = \int(\rho_A^{(1)}(1|1)\rho_A(2|1') - \rho_A^{(1)}(1|1')\rho_A(2|1) + \rho_A(1|1)\rho_A^{(1)}(2|1') - \rho_A(1|1')\rho_A^{(1)}(2|1)) \times \Lambda_B(1'2'|1'2)v(1,1')d\tau_1 d\tau_1' d\tau_2 d\tau_2',$$

$$\mathscr{X}_{cn}^{4A} = \int \Lambda_A^{(1)}(12|12')(\rho_B(1'|1')\rho_B(2'|2) - \rho_B(1'|2)\rho_B(2'|1')) \times v(1,1')d\tau_1 d\tau_1' d\tau_2 d\tau_2',$$

$$\mathscr{X}_{cc}^{4A} = \int \Lambda_A^{(1)}(12|12')\Lambda_B(1'2'|1'2)v(1,1')d\tau_1 d\tau_1' d\tau_2 d\tau_2'. \quad (18)$$

The terms from eqn (18) cannot be described as a product of two or more integrals, and are therefore size-extensive. A careful reader could notice that two terms in the integrand of $\mathscr{X}_n^{4A}$ are "missing", namely the contributions: $\rho_A^{(1)}(1|1)\rho_A(2|2')\rho_B(1'|1')\rho_B(2'|2)$ and $\rho_A(1|1)\rho_A^{(1)}(2|2')\rho_B(1'|1')\rho_B(2'|2)$. One can easily verify that these terms have served to remove the explicitly disconnected terms from eqn (10), since they give rise to $\bar{P}E_{\text{ind}}^{(2)}$ $(A \leftarrow B)$ and $E_{\text{elst}}^{(1)}\int \rho_A^{(1)}(2|2')\rho_B(2'|2)d\tau_2 d\tau_2'$ contributions, correspondingly. For convenience of the future discussion, the elements of eqn (17) can be divided into four separate groups, depending on the presence or absence of the cumulant. First of all, the terms $\mathscr{X}_n^{iA}$, $i = 1,2,3,4$, do not contain any cumulants, so the corresponding part of the exchange-induction energy will be denoted as $E_{\text{exch-ind}}^{(2)}(n)$ $(A \leftarrow B)$. From the remaining terms three groups can be distinguished, namely, those

containing the cumulant of the monomer $A(\mathscr{X}_c^{3A} + \mathscr{X}_{cn}^{4A})$, or of the monomer $B(\mathscr{X}_c^{2A} + \mathscr{X}_{nc}^{4A})$, or the cumulants of both monomers $(\mathscr{X}_{cc}^{4A})$. This partition is analogous to that recently proposed for the first-order exchange energy.[37]

III. Orbital formulae for the exchange-induction energy

The formulae presented in eqn (18) should be rewritten in an orbital form to allow for a practical implementation of the formalism. In the following the small letters p,q,r,s will denote the spinorbital indices, while the capital letters will stand for orbital indices. The Einstein convention of the summation over repeated indices is assumed.

The first-order density matrices of the monomer A can be expanded in a given spinorbital basis as,

$$\rho_A^{(1)}(1|1') = (\rho_A^{(1)})_q^p \phi^*_p(1)\phi_q(1'),$$

$$\Gamma_A^{(1)}(12|1'2') = (\Gamma_A^{(1)})_{q_1 q_2}^{p_1 p_2} \phi^*_{p_1}(1)\phi^*_{p_2}(2)\phi_{q_1}(1')\phi_{q_2}(2'). \quad (19)$$

The cumulant expansion in a given spinorbital basis can be obtained by exchanging $\Gamma_A^{(1)}$ to $\Lambda_A^{(1)}$ in the last equation. If the monomer wave functions Ψ_A and $\Psi_A^{(1)}$ are known, the expansion coefficients for $\rho_A^{(1)}$ and $\Gamma_A^{(1)}$ can be calculated from the formulae,

$$(\rho_A^{(1)})_q^p = \langle \Psi_A | e_q^p \Psi_A^{(1)} \rangle,$$

$$(\Gamma_A^{(1)})_{q_1 q_2}^{p_1 p_2} = \langle \Psi_A | e_{q_1 q_2}^{p_1 p_2} \Psi_A^{(1)} \rangle, \quad (20)$$

where $e_q^p = a^p a_q$ and $e_{q_1 q_2}^{p_1 p_2} = a^{p_1} a^{p_2} a_{q_2} a_{q_1}$ denote one- and two-particle spinorbital substitution operators[38,39] and a^p (a_p) stands for a creation (annihilation) operator of a spinorbital ϕ_p. For nonorthogonal basis sets also the overlap matrix will be utilized, with elements defined as $S_p^r = \int \phi^*_p(1)\phi_r(1)d\tau_1$. The analogous equations for zeroth-order density matrices of the monomer B can be obtained by interchanging indices A and B and by replacing first-order quantities by the zeroth-order ones. For the sake of simplicity the symbols $A_q^p = (\rho_A)_q^p$, $H_q^p = (\rho_A^{(1)})_q^p$ and $B_s^r = (\rho_B)_s^r$, will be used for the one-particle density matrices of monomers A and B.

When the summation over spin is performed, the orbital coefficients for density matrices and cumulants should be defined, too. For the closed-shell monomer it is convenient to introduce the following orbital quantities (where plus and minus denote the α and β spins),

$$A_Q^P = 2A_{Q+}^{P+},$$

$$(\Lambda_A^{(1)})_{SS'}^{RR'} = 2((\Lambda_A^{(1)})_{S+S'+}^{R+R'+} + (\Lambda_A^{(1)})_{S+S'-}^{R+R'-}). \quad (21)$$

Analogous definitions are used for other density matrices and cumulants. For the overlap matrix the orbital form $S_R^P = S_{R+}^{P+}$ is utilized.

For an effective coding it is advisable to express working formulae in terms of matrices, so that the standard linear algebra routines can be easily applied. Matrices of the dimensions $N \times N$, where N is the size of the atomic-orbital (AO) basis, will be denoted by bold capital letters, e.g. $(\mathbf{A})_Q^P = A_Q^P$. In the derivations of CCSD working orbital equations it was useful[40] to define Coulomb and exchange matrices for a given

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$N \times N$ matrix $\boldsymbol{X}$. For a concise notation in this paper it is desirable to use *generalized* right and left Coulomb matrices,

$$\overset{r}{\boldsymbol{J}}(\boldsymbol{X})_R^S = X_{S'}^{R'}(RS|v|R'S'),$$

$$\overset{l}{\boldsymbol{J}}(\boldsymbol{X})_{R'}^{S'} = X_S^R(RS|v|R'S'), \tag{22}$$

and *generalized* inner and outer exchange matrices,

$$\overset{i}{\boldsymbol{K}}(\boldsymbol{X})_R^{S'} = X_{S'}^{R'}(RS|v|R'S'),$$

$$\overset{o}{\boldsymbol{K}}(\boldsymbol{X})_{R'}^S = X_S^R(RS|v|R'S'). \tag{23}$$

These matrices were introduced in ref. 37, where an implementation of the first-order exchange energy in terms of cumulants was reported. In eqns (22) and (23) the 4-index integral

$$(PQ|v|RS) = \iint \phi_P^*(\boldsymbol{r}_1)\phi_Q(\boldsymbol{r}_2)v(\boldsymbol{r}_1,\boldsymbol{r}_2)\phi_R^*(\boldsymbol{r}_2)\phi_S(\boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2,$$

is utilized, where $\boldsymbol{r}$ denotes the spatial coordinates of an electron. The explicit form of the generalized Coulomb and exchange matrices was presented in ref. 37.

The technical details of the orbital expressions derivation for eqn (17) are similar to the case of the first-order exchange energy[37] and will be not repeated here. Summarizing, one should insert the expansion of one-particle density matrices into eqn (18), perform the summation over spin, and use eqns (21)–(23) to simplify the resulting expression. After some algebraic manipulations one gets the following formula for the noncumulant part of the exchange-induction energy,

$$
\begin{aligned}
E_{\text{exch-ind}}^{(2)}(n)(A \leftarrow B) = & -\frac{1}{2}\operatorname{tr}\left(\mathbf{H}^{\mathrm{T}}\overset{i}{\boldsymbol{K}}(\mathbf{B})\right) \\
& -\frac{1}{2}\operatorname{tr}\left((\mathbf{HSB})^{\mathrm{T}}\left[\overset{r}{\boldsymbol{J}}(\mathbf{B}) - \frac{1}{2}\overset{i}{\boldsymbol{K}}(\mathbf{B})\right]\right) \\
& -\frac{1}{2}\operatorname{tr}\left((\mathbf{BSA})\left[\overset{l}{\boldsymbol{J}}(\mathbf{H}) - \frac{1}{2}\overset{o}{\boldsymbol{K}}(\mathbf{H})\right]\right) \\
& -\frac{1}{2}\operatorname{tr}\left((\mathbf{BSH})\left[\overset{l}{\boldsymbol{J}}(\mathbf{A}) - \frac{1}{2}\overset{o}{\boldsymbol{K}}(\mathbf{A})\right]\right) \\
& +\frac{1}{4}\operatorname{tr}\left([(\mathbf{HSBSA}) + (\mathbf{ASBSH})]\overset{r}{\boldsymbol{J}}(\mathbf{B})\right) \\
& +\frac{1}{4}\operatorname{tr}\left((\mathbf{BSASB})\overset{l}{\boldsymbol{J}}(\mathbf{H})\right) \\
& +\frac{1}{4}\operatorname{tr}\left((\mathbf{BSHSB})\overset{l}{\boldsymbol{J}}(\mathbf{A})\right) \\
& -\frac{1}{8}\operatorname{tr}\left((\mathbf{HSB})^{\mathrm{T}}\overset{i}{\boldsymbol{K}}([\mathbf{BSA}]^{\mathrm{T}})\right) \\
& -\frac{1}{8}\operatorname{tr}\left((\mathbf{BSH})^{\mathrm{T}}\overset{o}{\boldsymbol{K}}(\mathbf{ASB})\right).
\end{aligned}
\tag{24}
$$

Note that eqn (24) is equivalent to the DFT-SAPT expressions for the second-order exchange-induction energy,[41] if Kohn–Sham (KS) and coupled-perturbed KS (CPKS) density

matrices are used in this formula. Analogously, if the self-consistent field (SCF) and CHF density matrices are inserted into eqn (24), the CHF exchange-induction energy (*i.e.* $E_{\text{exch-ind,resp}}^{(20)}$) results. The second-order induction energy can also be expressed in terms of density matrices and first-order density matrices,

$$E_{\text{ind}}^{(2)}(A \leftarrow B) = \operatorname{tr}\left(\mathbf{H}\overset{r}{\boldsymbol{J}}(\mathbf{B})\right). \tag{25}$$

The final formulae for the cumulant part of the $E_{\text{exch-ind}}^{(2)}$ $(B \leftarrow A)$ energy are listed below,

$$
\begin{aligned}
\mathscr{X}_c^{2A} + \mathscr{X}_{nc}^{4A} = \frac{1}{2}\Bigg\{ & \overset{l}{\boldsymbol{J}}(\boldsymbol{H})_R^S(\boldsymbol{SAS})_{R'}^{S'} \\
& + \overset{l}{\boldsymbol{J}}(\mathbf{A})_R^S(\boldsymbol{SHS})_{R'}^{S'} + \overset{l}{\boldsymbol{J}}(\boldsymbol{W}_{R'}^{S'})_R^S \Bigg\}(\varLambda_B)_{SS'}^{RR'},
\end{aligned}
\tag{26}
$$

$$
\begin{aligned}
\mathscr{X}_c^{3A} + \mathscr{X}_{cn}^{4A} = \frac{1}{2}(\varLambda_A^{(1)})_{QQ'}^{PP'} \\
\times \left\{ (\boldsymbol{SBS})_{P'}^{Q'}\overset{r}{\boldsymbol{J}}(\boldsymbol{B})_P^Q + \overset{r}{\boldsymbol{J}}(\boldsymbol{M}_{P'}^{Q'})_P^Q \right\},
\end{aligned}
\tag{27}
$$

$$\mathscr{X}_{cc}^{4A} = \frac{1}{2}(\varLambda_A^{(1)})_{QQ'}^{PP'}(\varLambda_B)_{SS'}^{RR'}\boldsymbol{S}_{P'}^{S'}\boldsymbol{S}_{R'}^{Q'}(PQ|v|RS), \tag{28}$$

where the quantities $W_{R'}^{S'}$ and $M_{P'}^{Q'}$ are given by the equations,

$$
\begin{aligned}
(\boldsymbol{W}_{R'}^{S'})_{Q'}^P &= (\boldsymbol{HS})_{R'}^P\delta_{Q'}^{S'} - \frac{1}{2}(\boldsymbol{HS})_{R'}^P(\boldsymbol{SA})_{Q'}^{S'} - \frac{1}{2}(\boldsymbol{AS})_{R'}^P(\boldsymbol{SH})_{Q'}^{S'}, \\
(\boldsymbol{M}_{P'}^{Q'})_{S'}^R &= (\boldsymbol{BS})_{P'}^R\delta_{S'}^{Q'} - \frac{1}{2}(\boldsymbol{BS})_{P'}^R(\boldsymbol{SB})_{S'}^{Q'}.
\end{aligned}
\tag{29}
$$

The $\boldsymbol{M}_{P'}^{Q'}$ matrix is exactly the same as for the case of the first-order exchange energy.[37] The $\boldsymbol{W}_{R'}^{S'}$ matrix differs from its counterpart from the first-order exchange-energy, since it contains the first-order density matrices of the monomer A.

The equations for the cumulant part of the $E_{\text{exch-ind}}^{(2)}$ $(B \leftarrow A)$ correction can be found analogously, if the following elements are interchanged: A and B indices, matrix elements for monomers A and B, left and right symbols over the generalized Coulomb matrices and outer and inner symbols over the generalized exchange matrices.

The computational cost of the equations above scales with the fourth, fifth, and sixth power of the dimension N of the orbital basis for eqns (24) and (26)–(28), respectively, if no restrictions in the summation ranges of indices are introduced. It should be stressed that the quantities $\boldsymbol{W}_{R'}^{S'}$ and $\boldsymbol{M}_{P'}^{Q'}$ are not constructed explicitly, since the calculation of N^2 generalized Coulomb matrices from precalculated $\boldsymbol{W}_{R'}^{S'}$ (or $\boldsymbol{M}_{P'}^{Q'}$) intermediates would increase the scaling of the computational time from $\mathcal{O}(N^5)$ to $\mathcal{O}(N^6)$.

IV. Exchange-induction energy in coupled cluster theory

The formulae derived so far are valid for any method, for which a cumulant decomposition of the reduced two-particle density matrices exists. In order to utilize eqns (24)–(28) for monomers described on the coupled cluster level, we need the expressions for the zeroth- and first-order density matrices and cumulants of coupled cluster theory. Since in this section only

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one monomer will be considered (say, monomer A), the subscript differentiating between monomers will be dropped.

A Ground-state coupled cluster density matrices and cumulants

The zeroth-order CC density matrices used in this paper are derived from the expectation value expression for the CC wave function, which has been presented by Jeziorski and Moszynski some time ago.[42] The authors of ref. 42 proposed to calculate the average value of an operator Y from the formula,

$$\bar{Y} = \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \rangle, \qquad (30)$$

resulting from the average-value expression $\bar{Y} = \langle \Psi | Y\Psi \rangle$ with the normalized CC wave function (T is the usual cluster excitation operator),

$$\Psi = \frac{e^T}{\langle e^{T^\dagger} e^T \rangle^{1/2}} \Phi. \qquad (31)$$

In the equations above Φ is the HF determinant (Fermi vacuum) and the shorthand notation $\langle Z \rangle = \langle \Phi | Z\Phi \rangle$ is utilized. An excitation operator S, $S = S_1 + S_2 + S_3 + \cdots$, introduced in ref. 42 and 43, is defined by the following expression,

$$e^S \Phi = \frac{e^{T^\dagger} e^T \Phi}{\langle e^{T^\dagger} e^T \rangle}. \qquad (32)$$

Note that the identity $\Phi = e^{-S^+}\Phi$ allows to put the operator $e^{-S^\dagger}$ in the r.h.s. of eqn (30). It has been proved in ref. 42 that the operator S is a connected quantity, as it can be expressed through a finite number of commutators of T and $T^\dagger$. From the connectedness of T and S it follows that eqn (30) is explicitly connected (provided that the operator Y is a connected quantity), since by the use of the nested commutator formula one can express $\bar{Y}$ as a sum of multiple commutators of connected quantities. It is equally important to notice that also approximate methods, that can be obtained from the expanded form of eqn (30) by neglecting some higher commutators, are connected and therefore size-extensive. In practice the S operator is always used in an approximate form. For instance, in CCSD theory one can put $S \approx T$, if one neglects terms of the $\mathcal{O}(W^3)$ order. The elements of one- and two-particle density matrices can be obtained from eqn (30) by inserting $Y = e_q^p$ or $Y = e_{q_1 q_2}^{p_1 p_2}$, correspondingly. The one-particle density matrix resulting from the CCSD wave functions has been derived and implemented recently[44] (the method presented in ref. 44 will be denoted here as the XCCSD-3 model).

A general formula for the CC cumulant has been presented in ref. 46. The somewhat complicated formula for the cumulant of the two-particle density matrix is given by the expression,[45]

$$\Lambda_{q_1 q_2}^{p_1 p_2} = \langle e^{S^\dagger} e^{-T} e_{q_1}^{p_1} e^T e^{-S^\dagger} \hat{\mathcal{2}} (e^{S^\dagger} e^{-T} e_{q_2}^{p_2} e^T e^{-S^\dagger}) \rangle \\ - \langle e^{S^\dagger} e^{-T} \tilde{e}_{q_1}^{p_2} e^T e^{-S^\dagger} \rangle \langle e^{S^\dagger} e^{-T} e_{q_2}^{p_1} e^T e^{-S^\dagger} \rangle, \qquad (33)$$

where $\tilde{e}_{q_1}^{p_2}$ is the one-hole substitution operator.[39] The superoperator $\hat{\mathcal{P}}$ is defined as $\hat{\mathcal{P}} = \hat{\mathcal{P}}_1 + \hat{\mathcal{P}}_2 + \cdots$, where $\hat{\mathcal{P}}_n(Z)$ projects the operator Z on the n-tuply excited space. It has

been demonstrated in ref. 45 that eqn (33) represents a connected, and therefore size-extensive quantity. As already mentioned, this cumulant has been used to obtain the first-order exchange energy with monomers described on the CCSD level.[37] (Note parenthetically that since Λ from eqn (33) has been derived from the N-electron wave function, it is obviously N-representable.[46]) It should be noted that the popular density matrices from gradient or linear-response coupled cluster (LR–CC) theory[47–49] cannot be used to define a cumulant, since the cumulant-like quantity obtained by inserting the LR–CC density matrices into eqn (15) contains disconnected terms.[45]

B First-order coupled cluster density matrices and cumulants

In the formula for the second-order exchange-induction energy the first-order density matrices and cumulants are also present. In order to obtain these quantities, the methods for calculating second-order molecular properties should be utilized. Again, the density matrices from LR–CC are unsuitable for the size-extensivity reasons and the expectation-value formulae should be used instead.

For the first-order wave function in CC theory the following ansatz can be proposed, which up to the multiplicative factor is identical with the expression for the first-order wave function in LR–CC and equation-of-motion CC (EOM–CC)[50,51] theories,

$$\Psi^{(1)} = (\Omega_0 + \Omega) \frac{e^T}{\langle e^{T^\dagger} e^T \rangle^{1/2}} \Phi, \qquad (34)$$

In this equation Ω_0 is a number, chosen to preserve the orthogonality of the $\Psi^{(1)}$ and Ψ wave functions, and Ω is an excitation operator which can be found by solving the usual equation for the first-order CC amplitudes,

$$[e^{-T} H e^T, \Omega] \Phi = -e^{-T} V_{\text{eff},B} e^T \Phi, \qquad (35)$$

in the space orthogonal to Φ. The same formula for the first-order cluster operator has been used in a recent study of the time-independent coupled-cluster polarization propagator.[52]

The general formula for the first-order density matrix can be obtained when the ansätze for the zeroth- and first-order wave functions (eqns (31) and (34)) are inserted into the expression $\langle \Psi | Y\Psi^{(1)} \rangle$ (where the spinorbital substitution operators are taken for the operator Y in order to obtain an element of the density matrix). After making use of the definition of the S operator (eqn (32)), one can write,

$$\langle \Psi | Y\Psi^{(1)} \rangle = \Omega_0 \langle e^{S^\dagger} e^{-T} Y e^T \rangle + \langle e^{S^\dagger} e^{-T} Y \Omega e^T \rangle. \qquad (36)$$

In the second step the identity $\hat{1} = e^{-S^\dagger} e^{S^\dagger}$ is inserted between the operators Y and Ω and the following property[52] of the superoperator $\hat{\mathcal{P}}$ is used: $Z\Phi = \langle Z \rangle \Phi + \hat{\mathcal{P}}(Z)\Phi$, to transform the r.h.s. of eqn (36) to the form,

$$\langle \Psi | Y\Psi^{(1)} \rangle = \Omega_0 \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \rangle + \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \rangle \\ \langle e^{S^\dagger} \Omega e^{-S^\dagger} \rangle + \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \hat{\mathcal{P}}(e^{S^\dagger} \Omega e^{-S^\dagger}) \rangle. \qquad (37)$$

From the orthogonality condition $\langle \Psi^{(1)} | \Psi \rangle = 0$ it follows that $\Omega_0 = -\langle e^{S^\dagger} \Omega e^{-S^\dagger} \rangle$, and finally the formula is obtained, which is identical with the first part of the formula for the polarization propagator from ref. 52,

$$\langle \Psi | Y \Psi^{(1)} \rangle = \langle e^{S^\dagger} e^{-T} Y e^T e^{-S^\dagger} \hat{\mathscr{P}} (e^{S^\dagger} \Omega e^{-S^\dagger}) \rangle. \qquad (38)$$

It should be noted that eqn (38) has already been implemented on the CCSD level for $Y = e_q^p$ (i.e. for the one-particle density matrix $\rho^{(1)}$) as an intermediate for the calculation of the time-independent CCSD propagator.[53]

It remains to be demonstrated how the two-particle first-order CC density matrix,

$$(\Gamma^{(1)})_{q_1 q_2}^{p_1 p_2} = \langle e^{S^\dagger} e^{-T} e_{q_1 q_2}^{p_1 p_2} e^T e^{-S^\dagger} \hat{\mathscr{Q}} (e^{S^\dagger} \Omega e^{-S^\dagger}) \rangle, \qquad (39)$$

can be divided into the antisymmetrized product of one-particle density matrices and the connected remainder, according to eqn (16). In the derivation process a similar method will be used as in ref. 45 for the ground-state CC cumulant.

Let us examine eqn (39) in more detail. It is obvious that one can always insert the identity $\hat{1} = e^T e^{-S^\dagger} e^{S^\dagger} e^{-T}$ between any two operators, e.g., between every creation and annihilation operator of the two-particle spinorbital substitution operator appearing in eqn (39),

$$(\Gamma^{(1)})_{q_1 q_2}^{p_1 p_2} = \langle e^{S^\dagger} e^{-T} a^{p_1} a^{p_2} a_{q_2} a_{q_1} e^T e^{-S^\dagger} \Theta \rangle$$

$$= \langle e^{S^\dagger} e^{-T} a^{p_1} e^T e^{-S^\dagger} e^{S^\dagger} e^{-T} a^{p_2} e^T e^{-S^\dagger} e^{S^\dagger} e^{-T} \qquad (40)$$

$$\times a_{q_2} e^T e^{-S^\dagger} e^{S^\dagger} e^{-T} a_{q_1} e^T e^{-S^\dagger} \Theta \rangle.$$

In eqn (40) the shorthand notation $\Theta = \hat{\mathscr{P}} (e^{S^\dagger} \Omega e^{-S^\dagger})$ has been used for the rightmost excitation operator appearing in eqn (39). If the following definitions are introduced,[45]

$$K^p = e^{S^\dagger} e^{-T} a^p e^T e^{-S^\dagger},$$

$$R_q = e^{S^\dagger} e^{-T} a_q e^T e^{-S^\dagger}, \qquad (41)$$

then the two-particle first-order density matrix can be rewritten in a short form as,

$$(\Gamma^{(1)})_{q_1 q_2}^{p_1 p_2} = \langle K^{p_1} K^{p_2} R_{q_2} R_{q_1} \Theta \rangle. \qquad (42)$$

Analogously, the one-particle zeroth- and first-order density matrices become

$$(\rho)_q^p = \langle e^{S^\dagger} e^{-T} a^p a_q e^T e^{-S^\dagger} \rangle = \langle K^p R_q \rangle,$$

$$(\rho^{(1)})_q^p = \langle e^{S^\dagger} e^{-T} a^p a_q e^T e^{-S^\dagger} \Theta \rangle = \langle K^p R_q \Theta \rangle. \qquad (43)$$

The operators K^{p_1} and K^{p_2} have an effective creation rank equal to one, whereas the operators R_{q_1} and R_{q_2} have an effective annihilation rank equal to one. These features reduce greatly a number of possible full contraction schemes between five operators from eqn (42), e.g. the pairs of operators like K^{p_1} and K^{p_2} or R_{q_2} and Θ cannot fully contract to a vacuum diagram. The analysis of possible contractions schemes reveals that the element $(\Gamma^{(1)})_{q_1 q_2}^{p_1 p_2}$ can be divided into five parts,

$$(\Gamma^{(1)})_{q_1 q_2}^{p_1 p_2} = \langle K^{p_1} K^{p_2} R_{q_2} R_{q_1} \Theta \rangle = \langle \{ K^{p_1} K^{p_2} R_{q_2} R_{q_1} \Theta \}_C \rangle$$

$$+ \langle K^{p_1} R_{q_1} \rangle \langle K^{p_2} R_{q_2} \Theta \rangle + \langle K^{p_2} R_{q_2} \rangle \langle K^{p_1} R_{q_1} \Theta \rangle$$

$$- \langle K^{p_2} R_{q_1} \rangle \langle K^{p_1} R_{q_2} \Theta \rangle - \langle K^{p_1} R_{q_2} \rangle \langle K^{p_2} R_{q_1} \Theta \rangle, \qquad (44)$$

where the subscript C denotes that all operators inside the curly parentheses are connected, i.e. joined by the summation

lines. The minus signs before the last two terms of eqn (44) appear because one needs an odd number of transpositions to arrive at the order of operators presented in those terms. The examination of eqn (44) reveals that the last four terms of this expression form the noncumulant part of the first-order two-particle density matrix in the partition introduced in eqn (16). The remaining part is connected by the way of construction. This shows that one can divide the first-order two-particle density matrix derived from the expectation-value formula for the coupled cluster wave function into the connected (and therefore size-extensive) cumulant part,

$$(\Lambda^{(1)})_{q_1 q_2}^{p_1 p_2} = \langle \{ K^{p_1} K^{p_2} R_{q_2} R_{q_1} \Theta \}_C \rangle, \qquad (45)$$

and the antisymmetrized products of zeroth- and first-order one-particle density matrices.

When the nested commutator formula is applied to eqns (41) and (45), numerous terms containing commutators of T and $S^\dagger$ operators will result, so the obtained expansion must be truncated for practical reasons. The importance of each term can be gauged by establishing its order in terms of the fluctuation operator W of the MP theory. In the truncation scheme,[52] used in this paper, a minimal number of terms is retained which contribute to the cumulant in a given MP order. A detailed analysis of orders of the perturbed amplitudes Ω with respect to the MP fluctuation operator has been performed in ref. 52. It turns out from this reference that the singly-excited operator Ω_1 gives a contribution already in the zeroth MP order (i.e. $\Omega_1 = \mathcal{O}(W^0)$), while the doubly-excited operator Ω_2 contributes in the first MP order (i.e. $\Omega_2 = \mathcal{O}(W^1)$). This feature of the Ω_1 operator should be confronted with the T_1 operator, which is of the $\mathcal{O}(W^2)$ order. Unfortunately, this also means that in order to include into the first-order cumulant all terms contributing on the $\mathcal{O}(W^2)$ level, also triply-excited amplitudes from CCSDT theory should be taken into account. Since the inclusion of triples will increase the cost of the calculations substantially, this study has been limited to the first nonvanishing cumulant order, i.e. only terms giving a contribution of the $\mathcal{O}(W^1)$ order are accounted for. An analysis of the expanded form of eqn (45) leads to the following spinorbital form of the first-order cumulant,

$$(\Lambda^{(1)})_{q_1 q_2}^{p_1 p_2} = \langle e_{q_1 q_2}^{p_1 p_2} \Omega_2 \rangle + \langle S_2^\dagger e_{q_1}^{p_1} \hat{\mathscr{Q}}_1 (e_{q_2}^{p_2} \Omega_1) \rangle$$

$$+ \langle S_2^\dagger e_{q_2}^{p_2} \hat{\mathscr{Q}}_1 (e_{q_1}^{p_1} \Omega_1) \rangle + \mathcal{O}(W^2). \qquad (46)$$

After performing the summation over spin the final working formulae for the first-order cumulant are obtained,

$$(\Lambda^{(1)})_{AB}^{IJ} = 4(2\Omega_{AB}^{IJ} - \Omega_{BA}^{IJ}),$$

$$(\Lambda^{(1)})_{IC}^{AB} = (\Lambda^{(1)})_{CI}^{BA} = 4(2S_{IJ}^{AB} - S_{IJ}^{BA})\Omega_C^J,$$

$$(\Lambda(1))_{IJ}^{AK} = (\Lambda^{(1)})_{JI}^{KA} = -4(2S_{IJ}^{AB} - S_{IJ}^{BA})\Omega_B^K. \qquad (47)$$

In eqn (47) I, J, K and A, B, C denote the occupied and virtual orbital indices (with respect to Φ) and the spin-free operators Ω_1, Ω_2, and $S_{2\dagger}$ are defined as,

$$\Omega_1 = \Omega_A^I E_I^A,$$

$$\Omega_2 = \tfrac{1}{2}\Omega_{AB}^{IJ} E_{IJ}^{AB},$$

$$S_2^\dagger = \tfrac{1}{2}S_{IJ}^{AB} E_{AB}^{IJ}, \qquad (48)$$

where E_J^A and E_{AB}^{IJ} are orbital substitution operators.[39] In order to treat both zeroth- and first-order cumulants on the same level, a similar formula is used also for the zeroth-order cumulant,[37]

$$\Lambda_{q_1 q_2}^{p_1 p_2} = \langle e_{q_1 q_2}^{p_1 p_2} T_2 \rangle + \langle S_2^\dagger e_{q_1 q_2}^{p_1 p_2} \rangle + \mathcal{O}(W^2), \qquad (49)$$

i.e. in comparison to the implementation of the first-order exchange energy[37] the cumulant contributions of order of $\mathcal{O}(W^2)$ are neglected here. Consequently, the $\mathscr{X}_{cc}^{4A}$ and $\mathscr{X}_{cc}^{4B}$ terms are skipped, as they contain two cumulants and give a contribution of the cumulative $\mathcal{O}(W^2)$ order.

C   Technical details

In both formulae (46) and (49) the converged T and Ω amplitudes from the CCSD theory are used. The one-particle zeroth- and first-order density matrices are the same as in ref. 45 (for the zeroth-order matrices) and ref. 53 (for the first-order matrices). In the latter case the so-called CCSD(3) model has been used for all cases with the exception of the helium dimer. For He$_2$ the CCSD(4) approach has been utilized instead, since it has been shown in ref. 53 that the latter model is practically exact (equivalent to FCI) for two-electron systems. The S_1 and S_2 operators are calculated up to terms containing three T and T operators.[52] In the formula for the $V_{\text{eff},B}$ potential the XCCSD-3 density of the monomer B is utilized.[44] It should be noted that because of the approximations made to the S operator the XCCSD-3 density is not symmetric. In the present work the symmetrized form of this density is used.

In order to distinguish between the general cumulant-containing quantities from eqn (18) and the approximate ones, with cumulants obtained from eqns (46) and (49), the latter will be denoted by a tilde. The second-order exchange-induction energy obtained from the formulae (24), (26) and (27) with coupled-cluster density matrices and cumulants described in the preceding paragraphs, will be denoted as $E_{\text{exch-ind}}^{(2)}(\text{XCCSD})$. Analogously, the second-order induction energy obtained with the same densities will be denoted as $E_{\text{ind}}^{(2)}(\text{XCCSD})$.

Summarizing, the second-order exchange-induction energy with the CCSD description of the monomers is calculated in this paper as a sum of the following contributions,

$$E_{\text{exch-ind}}^{(2)}(\text{XCCSD}) = E_{\text{exch-ind}}^{(2)}(n)(\text{XCCSD}) + \widetilde{\mathscr{X}}_{nc}^2 + \widetilde{\mathscr{X}}_{nc}^4 + \widetilde{\mathscr{X}}_{cn}^3 + \widetilde{\mathscr{X}}_{cn}^4. \qquad (50)$$

In this equation the contributions from $A \leftarrow B$ and $B \leftarrow A$ components of $E_{\text{exch-ind}}^{(2)}$ are given together, *e.g.* $\widetilde{\mathscr{X}}_{nc}^2 = \widetilde{\mathscr{X}}_{nc}^{2A} + \widetilde{\mathscr{X}}_{nc}^{2B}$.

The new formula has been implemented in a development version of the MOLPRO suite of programs.[54] The expression for the noncumulant part of the exchange-induction energy (24) can also be used to calculate the CHF and DFT exchange-induction energies, if the corresponding density matrices (SCF and CHF or KS and CPKS) are inserted into the formula instead of the coupled cluster density matrices. This fact has been used to verify the correctness of the new code. The cumulant part of the exchange-induction has, at it was already noticed, a similar form to the first-order exchange energy.

Actually, the same Fortran subroutines (with a few minor modifications) can be used to calculate both quantities.

V.   Results and discussion

The theory presented in the previous sections will be illustrated by calculations performed for several representative van der Waals complexes, such as: dimers of water, hydrogen fluoride, carbon monoxide, nitrogen molecule, ethyne, argon, and complexes of helium with water, helium with fluoride anion, and ethane with hydrogen cyanide. In all cases geometries near global minimum are used. For the He–F$^-$ complex the distance between the He and F atoms has been set to 5.6 a_0. For other complexes the geometries from references listed below have been used: (HF)$_2$,[55] (H$_2$O)$_2$,[55] (CO)$_2$,[56] (N$_2$)$_2$,[57] He–H$_2$O,[58] Ar$_2$,[59] C$_2$H$_6$–HCN[60] and (C$_2$H$_2$)$_2$ (the parallel-displaced geometry).[41] Some of those van der Waals molecules were previously utilized in studies on the correlated electrostatic,[44,61] first-order exchange,[37] induction,[23] and dispersion energies.[62] Additionally, the calculations for the helium dimer have been performed at various distances, used previously to calculate an accurate potential energy surface (PES) of He$_2$.[27,63] Most calculations reported in this paper were performed with the local development version of the MOLPRO suite of codes.[54] The calculations of the $^t E_{\text{ind}}^{(22)}$ correction and of the total SAPT interaction energy were performed with the SAPT program.[16] Finally, the DFT-SAPT results were obtained using the code developed by Hesselmann and Jansen,[64] which is a part of the MOLPRO suite of codes. In the DFT-SAPT calculations the PBE0 functional,[65,66] with an asymptotic correction proposed by Grüning *et al.*[67] was utilized for a description of monomers. The inner-shell orbitals (*i.e.* 1s for the C,N,O,F atoms and 1s2s2p for the Ar atom) were frozen in all CC calculations performed with the MOLPRO code. In the calculations made with the SAPT program all electrons were correlated.

The analysis of the performance of the new approach will be started from the case of the helium dimer. For this system the FCI induction and exchange-induction energies are available for a comparison.[27] Note that the helium dimer should be treated as a special case, since for the two-electron monomer the CCSD approach is exact (equivalent to FCI). In the method presented in this paper the noncumulant part of the exchange-induction energy is practically exact for He$_2$, since the one-particle density matrices used to calculate the induction energy and the noncumulant part of the exchange-induction energy in the XCCSD method differ from the FCI density matrices only by (i) neglecting terms containing more than three T and $T^\dagger$ operators in the definition of the S operator and, for the first-order density matrix, (ii) by truncating the multiple commutator expansion resulting from eqn (38) after the terms giving a contribution in the $\mathcal{O}(W^4)$ order (for details see ref. 53). Therefore, the main source of differences between the XCCSD and FCI exchange-induction energies for He$_2$ is the cumulant part of the former correction, since in the cumulant contributions the $\mathcal{O}(W^2)$ terms are neglected.

The induction and exchange-induction energies for the helium dimer are presented in Table 1. The FCI induction

Table 1 Second-order induction and exchange-induction energies in various approximations for the helium dimer. The DC147 basis[27,63] has been used. The second rows contain the percentage error with respect to the FCI exchange-induction energy (in the S^2 approximation). Energies are in μE_h, distances in a_0

R	3.0	3.5	4.0	4.5	5.0	5.3	5.6	6.0	7.0
$E_{\text{exch-ind,resp}}^{(2)}(\text{FCI})$	1331.8	319.80	76.361	18.269	4.3968	1.8770	0.80329	0.26004	0.015752
$E_{\text{exch-ind}}^{(20)}$	1144.6	277.07	65.541	15.454	3.6609	1.5479	0.65616	0.20976	0.012326
	−14.1	−13.4	−14.2	−15.4	−16.7	−17.5	−18.3	−19.3	−21.8
$E_{\text{exch-ind}}^{(2)}(\text{XCCSD})$	1258.9	315.48	76.527	18.416	4.4421	1.8975	0.81242	0.26485	0.015938
	−5.5	−1.4	0.2	0.8	1.0	1.1	1.1	1.9	1.2
$E_{\text{exch-ind}}^{(2)}(n)(\text{XCCSD})$	1201.9	295.98	71.032	16.970	4.0708	1.7340	0.74049	0.23903	0.014383
	−9.8	−7.4	−7.0	−7.1	−7.4	−7.6	−7.8	−8.1	−8.7
$\widetilde{\mathscr{X}}_c^3 + \widetilde{\mathscr{X}}_{cn}^4$	40.2	10.77	2.803	0.719	0.1837	0.0809	0.03561	0.01192	0.000774
$\widetilde{\mathscr{X}}_c^2 + \widetilde{\mathscr{X}}_{nc}^4$	−11.7	−1.02	−0.055	0.004	0.0019	0.0009	0.00035	0.00099	0.000004
$E_{\text{exch-ind}}^{(2)}(\text{DFT})$	1283.	304.6	70.54	16.34	3.820	1.605	0.6773	0.2156	0.01262
	−3.6	−4.7	−7.6	−10.5	−13.1	−14.5	−15.7	−17.1	−19.9
$^t E_{\text{exch-ind}}^{(2),\text{estim.}}(2)^a$	1168.6	283.90	67.437	15.976	3.8035	1.6132	0.68607	0.22028	0.013088
	−12.3	−11.2	−11.7	−12.6	−13.5	−14.0	−14.6	−15.3	−16.9
$E_{\text{exch-ind}}^{(2),\text{estim.}}(\text{XCCSD})^b$	1207.5	295.41	70.658	16.854	4.0397	1.7203	0.73449	0.23705	0.014264
	−9.3	−7.6	−7.5	−7.7	−8.1	−8.3	−8.6	−8.8	−9.4
$E_{\text{ind}}^{(2)}(\text{XCCSD})$	−1386.6	−333.94	−80.652	−19.605	−4.7998	−2.0697	−0.89437	−0.29305	−0.018232

^{a} $^t E_{\text{exch-ind, resp}}^{(2),\text{estim}}(2) = E_{\text{exch-ind, resp}}^{(20)} + {}^t E_{\text{exch-ind}}^{(22),\text{estim.}}$, where the second term is defined by eqn (3). ^{b} $E_{\text{exch-ind}}^{(2),\text{estim.}}(\text{XCCSD}) = \frac{E_{\text{exch-ind,resp}}^{(20)}}{E_{\text{ind,resp}}^{(20)}} E_{\text{ind}}^{(2)}(\text{XCCSD})$.

energy is not listed separately, as it is identical up to the last presented digit to the XCCSD induction energy. It turns out for this complex that the mean percentage error of the $E_{\text{exch-ind}}^{(2)}$ (XCCSD) energy with respect to the FCI exchange-induction energy is equal to 1.2%. This discrepancy can be attributed to the neglected terms in the zeroth- and first-order cumulants. It should be noted that for the case of the first-order exchange energy the $\mathcal{O}(W^2)$ cumulant contributes about 0.5–1% to the total first-order exchange energy,[37] which agrees with the order of magnitude of the error obtained for the XCCSD exchange-induction energy. The comparison with the listed values of the exchange-induction energies obtained by other available methods (DFT-SAPT, CHF, and CHF plus the correction estimated according to eqn (3)) allows to make a conclusion that the XCCSD approach gives results which are (with one exception) the closest to the FCI values. It should be noted that even the usage of the noncumulant part of the XCCSD exchange-induction energy (which is much cheaper in terms of computer time) gives a significant and systematic improvement over other approximate methods. It is also important to note that the contribution of the zeroth-order cumulant terms ($\widetilde{\mathscr{X}}_c^2 + \widetilde{\mathscr{X}}_{nc}^4$) is substantially larger than that of the first-order cumulant terms ($\widetilde{\mathscr{X}}_c^3 + \widetilde{\mathscr{X}}_{cn}^4$). Interestingly enough, the formula from eqn (3) with the $^t E_{\text{ind}}^{(22)}$ correction replaced by the XCCSD induction energy gives values that are very close to the noncumulant part of the XCCSD exchange-induction energy. Summarizing, the analysis of Table 1 allows to make the conclusion that a new method compares favorably to the exact FCI approach and is the best method available for a description of the electron correlation in the exchange-induction correction.

Exchange-induction energies for other test complexes are reported in Table 2. Also the CHF, DFT and XCCSD induction energies are listed there in order to assess the magnitude of damping of the polarization correction by its exchange counterpart. In order to facilitate the comparison, the correlation contributions for various methods, defined as $\varepsilon_{\text{exch-ind}}^{(2)}(\text{method}) = E_{\text{exch-ind}}^{(2)}(\text{method}) - E_{\text{exch-ind, resp}}^{(20)}$, are also

listed in the table. In order to allow for an analysis of the importance of various terms in eqn (50) all these components are separately listed in Table 2. The analysis of Table 2 shows that the noncumulant part of the exchange-induction gives the largest contribution to the correlation correction. For all molecules the $\varepsilon_{\text{exch-ind}}^{(2)}(n)(\text{XCCSD})$ component is larger than the $\varepsilon_{\text{exch-ind}}^{(2)}(c)(\text{XCCSD})$ term. For the case of polar molecules and dimers of argon, nitrogen molecule, and ethyne those two contributions differ by one order of magnitude. However, a couple of examples can be found in the table where those terms are of similar importance. It can also be noted that the zeroth-order cumulant (appearing in the sum $\widetilde{\mathscr{X}}_c^2 + \widetilde{\mathscr{X}}_{nc}^4$) gives the major part of the whole cumulant contribution for all examples considered, and that for some molecules the terms containing the first-order cumulant ($\widetilde{\mathscr{X}}_c^3 + \widetilde{\mathscr{X}}_{cn}^4$) give a negligible value. The contribution resulting from the first-order cumulant cannot be neglected for the interaction of two polar monomers, like a dimer of water. The largest difference between the CHF and XCCSD exchange-induction energies has been found for the complex of the helium atom with the fluoride anion. In this case the correlation contribution to the exchange-induction energy is larger than the CHF correction itself, whereas the induction correlation correction is only 13% lower than the $E_{\text{exch-ind, resp}}^{(20)}$ energy. As a result, estimated corrections are about 10 times too small in this case. It is interesting to note that the DFT-SAPT exchange-induction energy reproduces the XCCSD result reasonably well, although it is somewhat closer to the $E_{\text{exch-ind}}^{(2)}(n)(\text{XCCSD})$ contribution (the average errors of the DFT-SAPT exchange-induction energy for complexes from Table 2 constitute 5.5% with respect to the total $E_{\text{exch-ind}}^{(2)}(\text{XCCSD})$ energy and 4.4% for the noncumulant part, *i.e.* for $E_{\text{exch-ind}}^{(2)}(n)(\text{XCCSD})$).

It is interesting to note that for almost all complexes presented in Table 2, with the exception of the ethyne dimer and the complex of ethane with HCN, the correlation contributions to the induction and exchange-induction energies are negative and positive, respectively. For the ethyne dimer the signs of the correlation contributions are reversed,

Table 2 Second-order induction and exchange-induction energies for several van der Waals complexes in various approximations. For most cases the aug-cc-pVTZ basis has been used.[68,69] For the complex of helium with water the basis set from ref. 58 was taken. For dimers of H_2O, CO, N_2, and Ar the aug-cc-pVTZ basis was augmented with the 3s3p2d1f set on the midbond, as in, *e.g.*, ref. 23. All values in milliE_h

Molecule/correction	$(H_2O)_2$	$(HF)_2$	He–F⁻	$(CO)_2$	$(N_2)_2$	Ar_2	He–H_2O	$(C_2H_2)_2$	C_2H_6–HCN
$E^{(20)}_{\text{exch-ind, resp}}$	1.5105	1.8329	0.1177	0.1490	0.0608	0.2304	0.0097	0.6917	0.2687
$E^{(2)}_{\text{exch-ind}}(\text{XCCSD})$	2.0201	2.5546	0.2608	0.1774	0.0851	0.2653	0.0123	0.6101	0.3255
$E^{(2)}_{\text{exch-ind}}(n)(\text{XCCSD})$	1.9578	2.4992	0.2502	0.1661	0.0819	0.2607	0.0115	0.5738	0.3023
$E^{(2)}_{\text{exch-ind}}(\text{DFT})$	1.957	2.449	0.245	0.167	0.076	0.237	0.011	0.612	0.334
$^t E^{(2),\text{estim.}}_{\text{exch-ind}}(2)$	1.7111	2.1333	0.1272	0.1470	0.0726	0.2569	0.0099	0.6313	0.2606
$E^{(2)\text{estim}}_{\text{exch-ind}}(\text{XCCSD})$	1.7437	2.1901	0.1334	0.1636	0.0818	0.2627	0.0101	0.5770	0.2564
$\varepsilon^{(2)}_{\text{exch-ind}}(\text{XCCSD})$	0.5096	0.7217	0.1431	0.0284	0.0243	0.0349	0.0026	−0.0816	0.0568
$\varepsilon^{(2)}_{\text{exch-ind}}(\text{DFT})^a$	0.4469	0.6161	0.1272	0.0183	0.0153	0.0070	0.0012	−0.0801	0.0655
$^t E^{(22),\text{estim.}}_{\text{exch-ind}}{}^b$	0.2006	0.3004	0.0095	−0.0020	0.0118	0.0265	0.0002	−0.0605	−0.0082
$\varepsilon^{(2),\text{estim.}}_{\text{exch-ind}}(\text{XCCSD})^c$	0.2332	0.3572	0.0157	0.0146	0.0210	0.0324	0.0004	−0.1148	−0.0123
$\varepsilon^{(2)}_{\text{exch-ind}}(n)(\text{XCCSD})^d$	0.4474	0.6663	0.1325	0.0171	0.0211	0.0304	0.0018	−0.1179	0.0336
$\varepsilon^{(2)}_{\text{exch-ind}}(c)(\text{XCCSD})^e$	0.0623	0.0554	0.0106	0.0113	0.0032	0.0046	0.0007	0.0363	0.0232
$\widetilde{\mathscr{X}}^2_c + \widetilde{\mathscr{X}}^4_{nc}$	0.0855	0.0741	0.0126	0.0117	0.0034	0.0047	0.0007	0.0366	0.0227
$\widetilde{\mathscr{X}}^3_c + \widetilde{\mathscr{X}}^4_{cn}$	−0.0232	−0.0187	−0.0019	−0.0004	−0.0001	−0.0001	0.0000	−0.0003	0.0004
$E^{(20)}_{\text{ind,resp}}$	−3.0879	−3.9078	−0.7557	−0.1859	−0.0692	−0.2348	−0.0351	−0.9094	−0.9012
$E^{(2)}_{\text{ind}}(\text{DFT})$	−3.532	−4.585	−0.865	−0.201	−0.086	−0.242	−0.036	−0.790	−0.914
$E^{(2)}_{\text{ind}}(\text{XCCSD})$	−3.5647	−4.6694	−0.8565	−0.2041	−0.0932	−0.2679	−0.0365	−0.7585	−0.8598
$E_{\text{int}}(\text{MB–SAPT})^f$	−7.7406	−6.7992	−0.0529	−0.7568	−0.5293	−0.4907	−0.1599	−2.4424	−1.8069

$^a\ \varepsilon^{(2)}_{\text{exch-ind}}(\text{DFT}) = E^{(2)}_{\text{exch-ind}}(\text{DFT}) − E^{(20)}_{\text{exch-ind, resp}}$. $^b\ {}^t E^{(22),\text{estim.}}_{\text{exch-ind}}$ is calculated from the estimation formula (eqn (3)). $^c\ \varepsilon^{(2),\text{estim.}}_{\text{exch-ind}}(\text{XCCSD}) = E^{(2),\text{estim.}}_{\text{exch-ind}}(\text{XCCSD}) − E^{(20)}_{\text{exch-ind, resp}}$, where the formula for $E^{(2),\text{estim.}}_{\text{exch-ind}}(\text{XCCSD})$ is given in the footnote of Table 1. $^d\ \varepsilon^{(2)}_{\text{exch-ind}}(n)(\text{XCCSD}) = E^{(2)}_{\text{exch-ind}}(n)(\text{XCCSD}) − E^{(20)}_{\text{exch-ind, resp}}$. $^e\ \varepsilon^{(2)}_{\text{exch-ind}}(c)(\text{XCCSD}) = \widetilde{\mathscr{X}}^2_c + \widetilde{\mathscr{X}}^4_{nc} + \widetilde{\mathscr{X}}^3_c + \widetilde{\mathscr{X}}^4_{cn}$. ^{f} The total many-body (MB) SAPT interaction energy calculated as prescribed in ref. 3 and 16. For other terms see the footnotes of Table 1.

so the overall error, caused by neglecting the intramonomer electron correlation in the standard SAPT approach, is partially cancelled, as the sign of the estimated correction (eqn (3)) is correct. However, for the complex of ethane with HCN the correlation correction to the exchange-induction energy is also positive, and the estimated correction has a wrong sign in this case.

VI. Summary and conclusions

A new formulation of the second-order exchange-induction energy in the S^2 approximation has been proposed. The exchange-induction energy of the monomer A perturbed by the monomer B has been described with the use of the first-order interaction density matrix, which is constructed from one- and two-particle reduced density matrices of the monomer B and one- and two-particle first-order reduced density matrices of the monomer A. In analogy to the zeroth-order (*i.e.* ground-state) density matrices it has been proposed to separate the first-order two-particle density matrices into the antisymmetrized product of one-particle zeroth- and first-order density matrices and into two-particle first-order cumulant. Such an operation allows to divide the exchange-induction energy into a sum of two contributions: the non-cumulant part, built from the one-particle density matrices only, and the cumulant part. The orbital formulae for the new formulation of the exchange-induction energy have been derived. It has been demonstrated that the partition into the noncumulant and cumulant parts can be used for monomers described on the coupled cluster level, if first-order density matrices developed recently for the time-independent coupled

cluster propagator are utilized. The orbital formulae for cumulants were derived for monomers described by the coupled cluster singles and doubles wave functions, and for the cumulants truncated to the terms giving a contribution in the $\mathcal{O}(W^1)$ order. In this way the second-order exchange-induction energy with the inclusion of intramonomer correlation has been presented for the first time for many-electron systems. Numerical tests performed for the new formulation of the exchange-induction energy have shown that (i) the noncumulant part of the intramonomer correlation is always larger than the cumulant one, but still the cumulant contribution cannot be neglected, (ii) the first-order cumulant gives a very small contribution to the whole cumulant term, with the exception of interacting polar molecules or if a highly repulsive region of PES is considered. Summarizing, the presented level of calculation of the second-order exchange-induction energy should be sufficient for practical purposes. Possible extensions of the formalism would include the utilization of a more accurate zeroth-order cumulant as developed in ref. 37 and the implementation of the direct version of the code, which will allow to treat larger molecules and basis sets.

Acknowledgements

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