

Exchange-Dispersion Energy: A Formulation in Terms of Monomer Properties and Coupled Cluster Treatment of Intramonomer Correlation

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Abstract: A new formulation of the second-order exchange-dispersion energy of symmetry-adapted perturbation theory is presented. The proposed approach allows to study – for the first time for many-electron monomers – the effect of intramonomer electron correlation on this energy correction. In the new formalism the exchange-dispersion energy is expressed in terms of properties of interacting molecules, such as dynamic density-matrix susceptibilities and one-electron reduced density matrices. The resulting formula has been used to obtain the main (noncumulant) part of the exchange-dispersion energy for monomers described by coupled cluster theory limited to single and double excitations. A density fitting approach has been applied in order to reduce the computational effort for obtaining coupled cluster density-matrix susceptibilities. The new coupled cluster exchange-dispersion energy has been compared with other available values of this interaction energy component, obtained with monomers treated on the level of Hartree–Fock or density-functional theories.

1. Introduction

Symmetry-adapted perturbation theory (SAPT) (see refs 1–3 for reviews) is a well established alternative to the supermolecular approach for calculation of interaction energies between two closed-shell molecules A and B (called monomers in the following). In SAPT, one divides the total Hamiltonian H of a dimer AB into the unperturbed part H_0 , being the sum of monomers' Hamiltonians H_A and H_B , and a perturbation V , which describes the electrostatic interaction between monomers (N_A and N_B denote numbers of electrons in the monomers A and B, respectively):

$$V = \sum_{i=1}^{N_A} \sum_{j=1+N_A}^{N_A+N_B} \frac{1}{r_{ij}} - \sum_{i=1}^{N_A} \sum_{\beta \in B} \frac{Z_\beta}{r_{\beta i}} - \sum_{j=1+N_A}^{N_A+N_B} \sum_{\alpha \in A} \frac{Z_\alpha}{r_{\alpha j}} + \sum_{\alpha \in A} \sum_{\beta \in B} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (1)$$

The intermolecular interaction operator V can be conveniently rewritten in the form:

$$V = \sum_{i=1}^{N_A} \sum_{j=1+N_A}^{N_A+N_B} v(i, j) \quad (2)$$

where a generalized interaction operator $v(i, j)$ is defined as⁴

$$v(i, j) = \frac{1}{r_{ij}} - \frac{1}{N_B} \sum_{\beta \in B} \frac{Z_\beta}{r_{\beta i}} - \frac{1}{N_A} \sum_{\alpha \in A} \frac{Z_\alpha}{r_{\alpha j}} + \frac{1}{N_A N_B} \sum_{\alpha \in A} \sum_{\beta \in B} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (3)$$

[In the following the coordinates (including spin) of the i th electron will be denoted by a number i , while spatial coordinates of this electron will be defined as \mathbf{r}_i .]

In SAPT, the interaction energy up to the second order in V is defined as a sum of three Rayleigh–Schrödinger corrections: first-order electrostatic ($E_{\text{elst}}^{(1)}$), second-order induction ($E_{\text{ind}}^{(2)}$) and second-order dispersion ($E_{\text{disp}}^{(2)}$) energies and their exchange counterparts, accounting for electron tunneling effects between monomers: 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. In textbook derivations of perturbation theories it is always

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Table 1. The MP Level of SAPT(MP) Corrections (As Derived and Programmed in SAPT Program¹³)^a

energy	MP level	notes
$E_{\text{elst}}^{(1)}$	3	relaxed (preferred) and unrelaxed versions available. The fourth order is also present, although not used in practice
$E_{\text{ind}}^{(2)}$	2	unrelaxed version (<i>true</i> $E_{\text{ind}}^{(2)}$), ^{2,10} the relaxed version is available in the literature but absent in the SAPT program
$E_{\text{disp}}^{(2)}$	2	CCD+ST(CCD) ¹² dispersion energy is also available in SAPT; the coupled Hartree–Fock (CHF) dispersion energy also exists in the literature ¹⁸
$E_{\text{exch}}^{(1)}$	2	usually CCSD monomer amplitudes are used instead of MP1 and MP2 ones in formulas for the $E_{\text{exch}}^{(1)}$ energy components ¹¹
$E_{\text{exch-ind}}^{(2)}$	0	relaxed (preferred) and unrelaxed versions available, the scaling formula is used to estimate the intramonomer correlation effects
$E_{\text{exch-disp}}^{(2)}$	0	unrelaxed version

^a Some corrections are available in relaxed and unrelaxed versions, depending on whether monomer orbitals are or are not allowed to respond to the perturbation field of another monomer.

assumed that eigenvalues and eigenvectors of the H_0 part of the total Hamiltonian H are easy to calculate. However, it is well-known that the exact solutions of the zeroth-order Hamiltonian $H_0 = H_A + H_B$ are not available (with the exception of the smallest few-electron molecules). Therefore, additional approximations are necessary in order to obtain SAPT interaction energies for many-electron monomers.

Since usually the eigenfunctions of the Fock operator can be easily obtained, Hartree–Fock (HF) determinants are commonly used as a zeroth-order approximation to the unknown exact wave functions of monomers, giving rise to the SAPT(HF) approach. [A convention will be adopted in this paper to denote as SAPT(Z) the SAPT approach with monomers treated in the level Z.] Obviously, SAPT(HF) neglects the effect of Coulomb electron correlation inside the monomers. In order to account for this effect, every SAPT correction is expanded in terms of monomer fluctuation operators $W_X = H_X - F_X$, $X = A, B$, leading to the triple perturbation theory.⁵ Effectively, in this approach the Møller–Plesset (MP) expansion is utilized, so the method can be labeled as SAPT(MP).^{4,6–12} Energy corrections in SAPT(MP) are denoted as $E^{(nij)}$, where n , i and j are orders of the perturbation operators V , W_A , and W_B , respectively. The SAPT(MP) approach has been implemented into the SAPT suite of codes¹³ and has proven to be an efficient method for studying noncovalent complexes of small atoms and molecules (for examples of applications see refs 14–17). Levels of MP theory used for various SAPT corrections are presented in Table 1. In particular, it can be seen from this table that the exchange-dispersion energy in SAPT(MP) has been so far treated on the uncorrelated and uncoupled level (i.e., neither the electron correlation nor the orbital relaxation effects are taken into account for this correction). A lack of

the intramonomer correlation for the exchange-dispersion energy is potentially one of the main sources of errors in SAPT(MP).

Yet another treatment of the intramonomer correlation problem is based on a density-functional theory (DFT) description of monomers.^{19,20} Two groups were involved simultaneously in a development of SAPT(DFT): Misquitta, Szalewicz, and Jeziorski^{21,22} (see also ref 23) and Jansen and Hesselmann^{24–27} (the latter authors prefer to use the abbreviation DFT-SAPT for their method). The implementation of SAPT(DFT), followed by the utilization of the density fitting (DF) approximation²⁸ to electron-repulsion integrals,^{29–32} allows nowadays the use of SAPT for large van der Waals molecules, like dimers of cyclotrimethylene trinitramine³³ and DNA bases³⁴ or even for endohedral complexes of fullerenes.³⁵

Very recently a new SAPT(CC) approach has been proposed.^{36–42} In this method the wave functions of monomers are described by coupled cluster (CC) theory.⁴³ So far the CC treatment has been applied to the electrostatic,^{36,37} first-order exchange,^{40,41} induction,^{38,42} exchange-induction,⁴² and dispersion³⁹ terms. A new formalism proposed in this paper enables the calculation of the second-order exchange-dispersion energy with an account of intramonomer correlation. In practice, the method has been implemented for the case of monomers described by CC theory limited to single and double excitations (CCSD).

The plan for this paper is the following: first the exchange-dispersion energy will be expressed in terms of monomer properties in an explicitly connected form. Next the orbital working formula will be derived, and a DF approximation will be applied. Finally, the illustrative results for the CCSD exchange-dispersion energy will be presented and discussed.

2. Theory

2.1. Exchange-Dispersion Energy through Monomer Properties. The main goals of the derivations in the next sections are to describe the exchange-dispersion energy in terms of monomer properties and to express the resulting formula in a computationally convenient form.

It is known that if monomers are not too close to each other, then one can neglect multiple exchanges of electrons between them, what leads to the so-called single-exchange or S^2 approximation.⁴⁴ The second-order exchange-dispersion energy in the S^2 approximation is given by the following formula:^{45,46}

$$E_{\text{exch-disp}}^{(2)} = \langle \Psi_A^0 \Psi_B^0 | VP \Psi_{\text{disp}}^{(1)} \rangle - \bar{V} \langle \Psi_A^0 \Psi_B^0 | P \Psi_{\text{disp}}^{(1)} \rangle - \bar{P} \langle \Psi_A^0 \Psi_B^0 | V \Psi_{\text{disp}}^{(1)} \rangle \quad (4)$$

In eq 4, Ψ_A^0 and Ψ_B^0 are the exact wave functions for the ground states of the monomers A and B, and P denotes the single-exchange operator:

$$P = - \sum_{i=1}^{N_A} \sum_{j=1+N_A}^{N_A+N_B} P_{ij} \quad (5)$$

while the first-order dispersion wave function is obtained from the following equation:

$$\Psi_{\text{disp}}^{(1)} = - \sum_{K=1}^{\infty} \sum_{L=1}^{\infty} \frac{|\Psi_A^K \Psi_B^L \rangle \langle \Psi_A^K \Psi_B^L | V_{\text{ee}} | \Psi_A^0 \Psi_B^0 \rangle}{\Delta E_A^K + \Delta E_B^L} \quad (6)$$

where indices $K(L)$ number the eigenstates of the monomer A(B), ΔE_A^K and ΔE_B^L denote excitation energies of the monomers A and B from their ground states, and V_{ee} is a pure two-electron part of the operator V . Finally, the symbol \bar{X} denotes the mean value of an operator X with the zeroth-order wave function, i.e., with $\Psi_A^0 \Psi_B^0$ (so, e.g. $\bar{V} = E_{\text{elst}}^{(1)}$).

Let us consider the term:

$$-\langle \Psi_A^0 \Psi_B^0 | VP \Psi_A^K \Psi_B^L \rangle = \int \Psi_A^0(1, 2, \dots, N_A) * \Psi_B^0(1', 2', \dots, N'_B) * \sum_{i=1}^{N_A} \sum_{i'=1'}^{N'_B} v(i, i') \times \sum_{j=1}^{N_A} \sum_{j'=1'}^{N'_B} P_{jj'} \Psi_A^K(1, 2, \dots, N_A) \Psi_B^L(1', 2', \dots, N'_B) d\tau_1 \dots d\tau_{N_B} \quad (7)$$

which is obtained when eq 6 is inserted into eq 4 (electrons of the monomer B are denoted by primes, i.e., $i' = i + N_A$). After making use of the indistinguishability of electrons within the monomers the following four types of integrals are obtained from eq 7:

$$\begin{aligned} -\langle \Psi_A^0 \Psi_B^0 | VP \Psi_A^K \Psi_B^L \rangle &= N_A N_B \int \Psi_A^0(1, 2, \dots, N_A) * \Psi_B^0(1', 2', \dots, N'_B) * v(1, 1') \\ &\times [\Psi_A^K(1', 2, \dots, N_A) \Psi_B^L(1, 2', \dots, N'_B) \\ &+ (N_B - 1) \Psi_A^K(2', 2, \dots, N_A) \Psi_B^L(1', 1, \dots, N'_B) \\ &+ (N_A - 1) \Psi_A^K(1, 1', \dots, N_A) \Psi_B^L(2, 2', \dots, N'_B) \\ &+ (N_A - 1)(N_B - 1) \Psi_A^K(1, 2', \dots, N_A) \Psi_B^L(1', 2, \dots, N'_B)] d\tau_1 \dots d\tau_{N_B} \end{aligned} \quad (8)$$

In eq 8, the reduced one- and two-electron transition density matrices from the ground to the K th (L th) excited state of the monomer A(B) can be identified. For the monomer A, these transition density matrices are given by the formulas,

$$\begin{aligned} \rho_A^{0 \rightarrow K}(1|1') &= N_A \int \Psi_A^0(1, 2, \dots, N_A) * \Psi_A^K(1', 2, \dots, N_A) d\tau_2 \dots d\tau_{N_A} \\ \Gamma_A^{0 \rightarrow K}(12|1'2') &= N_A(N_A - 1) \int \Psi_A^0(1, 2, \dots, N_A) * \Psi_A^K(1', 2', \dots, N_A) d\tau_3 \dots d\tau_{N_A} \end{aligned} \quad (9)$$

Note that the ground-state density matrices $\rho_A(1|1')$ and $\Gamma_A(12|1'2')$ can be obtained by replacing Ψ_A^K by Ψ_A^0 in eq 9. The definitions from eq 9 allow us to rewrite the term under study in the following way:

$$\begin{aligned} -\langle \Psi_A^0 \Psi_B^0 | VP \Psi_A^K \Psi_B^L \rangle &= \int \rho_A^{0 \rightarrow K}(1|1') \rho_B^{0 \rightarrow L}(1'|1) v(1, 1') d\tau_1 d\tau'_1 \\ &+ \int \rho_A^{0 \rightarrow K}(1|2') \Gamma_B^{0 \rightarrow L}(1'2'|1'1) v(1, 1') d\tau_1 d\tau'_1 d\tau'_2 \\ &+ \int \Gamma_A^{0 \rightarrow K}(12|1'1') \rho_B^{0 \rightarrow L}(1'1|2) v(1, 1') d\tau_1 d\tau'_1 d\tau_2 \\ &+ \int \Gamma_A^{0 \rightarrow K}(12|1'2') \Gamma_B^{0 \rightarrow L}(1'2'|1'2) v(1, 1') d\tau_1 d\tau'_1 d\tau_2 d\tau'_2 \end{aligned} \quad (10)$$

An analogous derivation for the integral present in the numerator of eq 6 leads to a similar result,

$$\langle \Psi_A^K \Psi_B^L | V_{\text{ee}} | \Psi_A^0 \Psi_B^0 \rangle = \int \rho_A^{K \rightarrow 0}(1|1) \rho_B^{L \rightarrow 0}(1'|1') \frac{1}{r_{11'}} d\tau_1 d\tau'_1 \quad (11)$$

The final step needed to rewrite eq 4 through quantities belonging to the monomers A and B, is performed by utilizing the equation for energy denominators:

$$\frac{1}{\Delta E_A^K + \Delta E_B^L} = \frac{2}{\pi} \int_0^\infty \frac{\Delta E_A^K}{(\Delta E_A^K)^2 + \omega^2} \frac{\Delta E_B^L}{(\Delta E_B^L)^2 + \omega^2} d\omega \quad (12)$$

used by Longuet-Higgins⁴⁷ to derive his famous formula for the second-order dispersion energy in terms of frequency-dependent density susceptibilities of the monomers A and B, $\alpha_X(\mathbf{r}, \mathbf{r}'; \omega)$:

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_0^\infty \int \alpha_A(\mathbf{r}_1, \mathbf{r}_2; i\omega) \alpha_B(\mathbf{r}_3, \mathbf{r}_4; i\omega) \frac{1}{r_{13}} \frac{1}{r_{24}} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 d\omega \quad (13)$$

By combining eqs 4, 10, 11, and 12, one expresses the exchange-dispersion energy in terms of monomer properties, at the cost of making an integration over the frequency ω . The monomer properties, which have been identified in this process, are straightforward generalizations of frequency-dependent density susceptibilities and will be denoted as density-matrix susceptibilities α and $\tilde{\alpha}$. For imaginary frequencies (the only ones which are of interest in the context of this work), these two new quantities are defined through transition density matrices and excitation energies in the following way:

$$\alpha_A(111'; 2li\omega) = 2 \sum_{K=1}^\infty \rho_A^{0 \rightarrow K}(111') \rho_A^{K \rightarrow 0}(2|2) \frac{\Delta E_A^K}{(\Delta E_A^K)^2 + \omega^2} \quad (14)$$

$$\tilde{\alpha}_A(121'2'; 3li\omega) = 2 \sum_{K=1}^\infty \Gamma_A^{0 \rightarrow K}(121'2') \rho_A^{K \rightarrow 0}(3|3) \frac{\Delta E_A^K}{(\Delta E_A^K)^2 + \omega^2} \quad (15)$$

(For the monomer B, the definitions are completely analogous).

It is noteworthy that the density-matrix susceptibility α can be defined in a way that is independent of the sum-over-state expansion (eq 14). To this end, a quantity related to the polarization propagator, which will be denoted as a “half-propagator” $\langle\langle X; Y \rangle\rangle_{i\omega}^+$ should be defined for operators X and Y (the Y operator should be Hermitian):

$$\langle\langle X; Y \rangle\rangle_{i\omega}^+ = -2 \langle \Psi_0 | X \text{Re} \frac{Q}{H - E_0 - i\omega} Y | \Psi_0 \rangle \quad (16)$$

where $Q = 1 - |\Psi_0\rangle\langle\Psi_0|$ is the projection on the space orthogonal to Ψ_0 . Then the density-matrix susceptibility can be defined as

$$\alpha(111'; 2li\omega) = -\langle\langle \hat{\rho}(111'); \hat{\rho}(2) \rangle\rangle_{i\omega}^+ \quad (17)$$

where $\hat{\rho}(1)$ and $\hat{\rho}(111')$ are the electron density and density-matrix operators. In the algebraic approximation these operators are given by the equations:

$$\begin{aligned} \hat{\rho}(1) &= \sum_{pq} \phi_p^*(1) \phi_q(1) \hat{e}_q^p \\ \hat{\rho}(111') &= \sum_{pq} \phi_p^*(1) \phi_q(1') \hat{e}_q^p \end{aligned} \quad (18)$$

The operator $\hat{e}_q^p = a^p a_q$ entering eq 18 denotes the usual spinorbital replacement operator⁴⁸ (a^p and a_p are the creation and annihilation operators for the spinorbital ϕ_p). In the following, real spinorbitals will be assumed. It can be noted that a usual density susceptibility $\alpha(1, 2li\omega)$ is obtained from eq 17 if $1 = 1'$ is set.

After making use of definitions from eqs 14 and 15, the second-order exchange-dispersion energy can be expressed as

$$\begin{aligned} E_{\text{exch-disp}}^{(2)} &= \frac{1}{2\pi} \int_0^\infty \int \alpha_A(111'; 3li\omega) \alpha_B(1'11; 3'li\omega) v(1, 1') \frac{1}{r_{33'}} d\tau_1 d\tau_1' d\tau_3 d\tau_3' d\omega \\ &+ \frac{1}{2\pi} \int_0^\infty \int \alpha_A(112'; 3li\omega) \tilde{\alpha}_B(1'2'11'; 3'li\omega) v(1, 1') \frac{1}{r_{33'}} d\tau_1 d\tau_1' d\tau_2 d\tau_3 d\tau_3' d\omega \\ &+ \frac{1}{2\pi} \int_0^\infty \int \tilde{\alpha}_A(1211'; 3li\omega) \alpha_B(1'12; 3'li\omega) v(1, 1') \frac{1}{r_{33'}} d\tau_1 d\tau_1' d\tau_2 d\tau_3 d\tau_3' d\omega \\ &+ \frac{1}{2\pi} \int_0^\infty \int \tilde{\alpha}_A(1212'; 3li\omega) \tilde{\alpha}_B(1'2'11'2'; 3'li\omega) v(1, 1') \frac{1}{r_{33'}} d\tau_1 d\tau_1' d\tau_2 d\tau_2' d\tau_3 d\tau_3' d\omega \\ &- E_{\text{elst}}^{(1)} \frac{1}{2\pi} \int_0^\infty \int \alpha_A(212'; 3li\omega) \alpha_B(2'12; 3'li\omega) \frac{1}{r_{33'}} d\tau_2 d\tau_2' d\tau_3 d\tau_3' d\omega \\ &+ \bar{P} \frac{1}{2\pi} \int_0^\infty \int \alpha_A(212; 3li\omega) \alpha_B(2'12'; 3'li\omega) v(2, 2') \frac{1}{r_{33'}} d\tau_2 d\tau_2' d\tau_3 d\tau_3' d\omega \end{aligned} \quad (19)$$

Equation 19 describes the exchange-dispersion energy in terms of monomer properties, analogously to the Longuet-Higgins formula for the dispersion energy.

2.2. Explicitly Connected Formula for the Exchange-Dispersion Energy. Equation 19 contains two explicitly disconnected terms (the last two terms), and it is not clear from the form of this expression if they cancel with some parts of the main term (they *should* cancel since the exchange-dispersion energy is size-extensive). In order to perform the explicit cancellation, the concept of the transition density cumulant is utilized. The cumulant of the transition density matrix has been introduced in ref 42 where it has served to remove explicitly disconnected parts in the formula for the second-order exchange-induction energy. Two-electron transition density matrices Γ^{0-K} can be divided into five additive parts: four products of one-electron transition and ground-state density matrices and a size-extensive cumulant part:

$$\Gamma^{0-K}(12|1'2') = \rho^{0-K}(1|1')\rho(2|2') - \rho^{0-K}(1|2')\rho(2|1') + \rho(1|1')\rho^{0-K}(2|2') - \rho(1|2')\rho^{0-K}(2|1') + \Lambda^{0-K}(12|1'2') \quad (20)$$

The specific formulas for quantities given in eq 20 can be obtained in the algebraic approximation if the matrices Γ^{0-K} and ρ^{0-K} are expanded according to eqs 19 and 20 of ref 42. From eq 20 it follows that the $\tilde{\alpha}$ density-matrix susceptibility can be also decomposed into the same number of components. Four of these terms are constructed from products of the α density-matrix susceptibility and one-electron density matrices, while the fifth term is a true two-electron part of $\tilde{\alpha}$, so it will be named a *cumulant susceptibility* and denoted as λ :

$$\tilde{\alpha}(12|1'2';3|i\omega) = \alpha(1|1';3|i\omega)\rho(2|2') - \alpha(1|2';3|i\omega)\rho(2|1') + \alpha(2|2';3|i\omega)\rho(1|1') - \alpha(2|1';3|i\omega)\rho(1|2') + \lambda(12|1'2';3|i\omega) \quad (21)$$

[Note parenthetically that if the summation in eq 15 is performed over Hartree–Fock determinants, then it is restricted to singly excited configurations, so that the quantity λ in this case is equal to zero.] The partition given in eq 21 can be utilized to divide $E_{\text{exch-disp}}^{(2)}$ into the part containing only α 's and ρ 's (this part will be denoted as “(n)”), and the rest, having at least one cumulant-like quantity λ (denoted as “(c)”). Two terms resulting from the fourth integral of eq 19 cancel with the explicitly disconnected terms, analogously as in the approach used in ref 42 for the exchange-induction energy. The remaining expression for the exchange-dispersion energy does not contain products of integrals and is, therefore, explicitly size-extensive, provided that proper (i.e., size-extensive) density-matrix susceptibilities are utilized. For a brevity of the next formula for the exchange-dispersion energy, the following notation will be introduced: if a product $f(ij)g(kl)$ of functions f and g depending on electron coordinates i,j,k,l is given, then the symbol π_{ik}^* permutes the coordinates of f and g placed just before the vertical bar, while π_{jl} permutes the electron coordinates just after the vertical bar. Additionally, the symbols $\mathcal{A}_{ik}^* = 1 - \pi_{ik}^*$ and $\mathcal{A}_{jl} = 1 - \pi_{jl}$ will be defined. Then, e.g., $\pi_{12}\alpha(1|1';3|i\omega)\rho(2|2') = \alpha(1|2';3|i\omega)\rho(2|1')$, while $\pi_{12}^*\alpha(1|1';3|i\omega)\rho(2|2') = \alpha(2|1';3|i\omega)\rho(1|2')$. Finally, let π_{ij}^X and \mathcal{A}_{ij}^X (with or without an asterisk) denote symbols acting on electron coordinates of α_X and ρ_X only ($X = A, B$). These symbols will generate the parts of the formula for the exchange-dispersion energy, which have not been written explicitly for the sake of conciseness. With these definitions, the explicitly connected formulas for the noncumulant part of the exchange-dispersion energy can be written in the following compact form:

$$\begin{aligned} E_{\text{exch-disp}}^{(2)}(\text{n}) = & \frac{1}{2\pi} \int_0^\infty \int \alpha_A(1|1';3|i\omega)\alpha_B(1'|1;3'|i\omega)v(1,1')\frac{1}{r_{33'}}d\tau_1d\tau_1'd\tau_3d\tau_3'd\omega \\ & + \frac{1}{2\pi} \int_0^\infty \int v(1,1')\alpha_A(1|2';3|i\omega)\mathcal{A}_{12'}^{*B}\mathcal{A}_{1'1}^B\alpha_B(1'|1';3'|i\omega)\rho_B(2'|1)\frac{1}{r_{33'}}d\tau_1d\tau_1'd\tau_2'd\tau_3'd\omega \\ & + \frac{1}{2\pi} \int_0^\infty \int v(1,1')\mathcal{A}_{12}^{*A}\mathcal{A}_{11'}^A\alpha_A(1|1';3|i\omega)\rho_A(2|1')\alpha_B(1'|2';3'|i\omega)\frac{1}{r_{33'}}d\tau_1d\tau_1'd\tau_2'd\tau_3'd\omega \\ & + \frac{1}{2\pi} \int_0^\infty \int v(1,1')(\mathcal{A}_{12}^{*A}\mathcal{A}_{12'}^A\mathcal{A}_{12'}^{*B}\mathcal{A}_{1'2}^B - 1 - \pi_{12}^{*A}\pi_{12}^A\pi_{12'}^{*B}\pi_{1'2}^B)\alpha_A(1|1';3|i\omega)\rho_A(2|2') \\ & \times \alpha_B(1'|1';3'|i\omega)\rho_B(2'|2)\frac{1}{r_{33'}}d\tau_1d\tau_1'd\tau_2'd\tau_3'd\omega \end{aligned} \quad (22)$$

Similarly, the cumulant-containing part is given by the following expression:

$$\begin{aligned} E_{\text{exch-disp}}^{(2)}(\text{c}) = & \frac{1}{2\pi} \int_0^\infty \int \alpha_A(1|2';3|i\omega)\lambda_B(1'2'|1'1;3'|i\omega)v(1,1')\frac{1}{r_{33'}}d\tau_1d\tau_1'd\tau_2'd\tau_3'd\omega \\ & + \frac{1}{2\pi} \int_0^\infty \int \lambda_A(12|12';3|i\omega)\alpha_B(1'|2';3'|i\omega)v(1,1')\frac{1}{r_{33'}}d\tau_1d\tau_1'd\tau_2'd\tau_3'd\omega \\ & + \frac{1}{2\pi} \int_0^\infty \int v(1,1')(\mathcal{A}_{12}^{*A}\mathcal{A}_{12'}^A\alpha_A(1|1';3|i\omega)\rho_A(2|2')\lambda_B(1'2'|1'2;3'|i\omega) \\ & + \lambda_A(12|11';3|i\omega)\mathcal{A}_{12'}^{*B}\mathcal{A}_{1'2}^B\alpha_B(1'|1';3'|i\omega)\rho_B(2'|2) \\ & + \lambda_A(12|11';3|i\omega)\lambda_B(1'2'|1'2;3'|i\omega))\frac{1}{r_{33'}}d\tau_1d\tau_1'd\tau_2'd\tau_3'd\omega \end{aligned} \quad (23)$$

Equations 22 and 23 are the main formulas of the first part of this paper.

It can be noted that a similar procedure can be employed to express the exchange-induction energy through static density-matrix susceptibilities of monomers. The corresponding formula is given in the Appendix Section.

2.3. Spinorbital Form of $E_{\text{exch-disp}}^{(2)}$. For practical applications, the formulas presented in eqs 22 and 23 should be rewritten in the algebraic approximation. If a spinorbital basis $\{\phi_p\}$ is used, then the expansions of one-electron density matrices and transition density matrices for the monomer A take the form:

$$\rho_A(1|2) = \sum_{pq} (\rho_A)_q^p \phi_p^*(1) \phi_q(2) \quad (24)$$

$$\rho_A^{0 \rightarrow K}(1|2) = \sum_{pq} (\rho_A^{0 \rightarrow K})_q^p \phi_p^*(1) \phi_q(2) \quad (25)$$

where the expansion coefficients can be found from the following expressions:

$$\begin{aligned} (\rho_A)_q^p &= \langle \Psi_A^0 | \hat{e}_q^p \Psi_A^0 \rangle \\ (\rho_A^{0 \rightarrow K})_q^p &= \langle \Psi_A^0 | \hat{e}_q^p \Psi_A^K \rangle \end{aligned} \quad (26)$$

The expressions for the monomer B are obtained by replacing the index A by B.

An expansion of the density-matrix susceptibility in a spinorbital basis leads to the following expression (we skip the index A):

$$\alpha(1|2;3|i\omega) = \sum_{p_1 q_1} \sum_{p_2 q_2} \Pi_{q_1 q_2}^{p_1 p_2}(i\omega) \phi_{p_1}^*(1) \phi_{q_1}(2) \phi_{p_2}^*(3) \phi_{q_2}(3) \quad (27)$$

where coefficients $\Pi_{q_1 q_2}^{p_1 p_2}(i\omega)$ are defined as

$$\Pi_{q_1 q_2}^{p_1 p_2}(i\omega) = 2 \sum_{K=1} (\rho^{0 \rightarrow K})_{q_1}^{p_1} (\rho^{K \rightarrow 0})_{q_2}^{p_2} \frac{\Delta E^K}{(\Delta E^K)^2 + \omega^2} \quad (28)$$

If real spinorbitals are considered, the remaining permutational symmetry of spinorbital indices p_2 and q_2 in eq 27 allows to rewrite the coefficients in the following form:

$$\Pi_{q_1 q_2}^{p_1 p_2}(i\omega) = -\langle \langle \hat{e}_{q_1}^{p_1}; \hat{e}_{q_2}^{p_2} \rangle \rangle_{i\omega}^+ \quad (29)$$

where $\hat{g}_{q_2}^{p_2} = (1/2)(\hat{e}_{q_2}^{p_2} + \hat{e}_{p_2}^{q_2})$. In practice, these coefficients can be obtained by a slight modification of the algorithm for the calculation of the polarization propagators.

Six-index expansion coefficients for the cumulant susceptibilities can be defined analogously to eq 28:

$$\Lambda_{q_1 q_2 q_3}^{p_1 p_2 p_3}(i\omega) = 2 \sum_{K=1} (\Lambda^{0 \rightarrow K})_{q_1 q_2}^{p_1 p_2} (\rho^{K \rightarrow 0})_{q_3}^{p_3} \frac{\Delta E^K}{(\Delta E^K)^2 + \omega^2} \quad (30)$$

(for a definition of the $(\Lambda^{0 \rightarrow K})_{q_1 q_2}^{p_1 p_2}$ expansion coefficients in eq 30 see ref 42). To proceed further let us introduce the following permutation operator:

$$P_{p_1 p_2, q_1 q_2} = (1 - P_{p_1 p_2})(1 - P_{q_1 q_2}) \quad (31)$$

where P_{rs} permutes spinorbital indices r and s , and a “chemical” notation for generalized two-electron integrals is used

$$(pq|v|rs) = \int \phi_p^*(1) \phi_q(1) v(1, 2) \phi_r^*(2) \phi_s(2) d\tau_1 d\tau_2 \quad (32)$$

A pure two-electron repulsion integral is denoted as

$$(pq|rs) = \int \phi_p^*(1) \phi_q(1) \frac{1}{r_{12}} \phi_r^*(2) \phi_s(2) d\tau_1 d\tau_2 \quad (33)$$

Combining eqs 24, 27, 32, and 33, one can transform the noncumulant part of the exchange-dispersion energy to the following spinorbital form:

$$\begin{aligned}
E_{\text{exch-disp}}^{(2)}(\mathbf{n}) = & \frac{1}{2\pi} \left\{ \int_0^\infty \hat{\Pi}_{q_1 q_3}^{p_1 p_3}(i\omega) \hat{\Pi}_{s_1 s_3}^{r_1 r_3}(i\omega) d\omega (p_1 s_1 | v | r_1 q_1) \right. \\
& + (p_1 s_2 | v | r_1 s_1) S_{r_2}^{q_1} P_{r_1 r_2, s_1 s_2} \int_0^\infty \hat{\Pi}_{q_1 q_3}^{p_1 p_3}(i\omega) \hat{\Pi}_{s_2 s_3}^{r_2 r_3}(i\omega) d\omega (\rho_B)_{s_1}^{r_1} \\
& + (p_1 q_1 | v | r_1 q_2) S_{p_2}^{s_1} P_{p_1 p_2, q_1 q_2} \int_0^\infty \hat{\Pi}_{q_2 q_3}^{p_2 p_3}(i\omega) \hat{\Pi}_{s_1 s_3}^{r_1 r_3}(i\omega) d\omega (\rho_A)_{q_1}^{p_1} \\
& + (p_1 q_1 | v | r_1 s_1) S_{p_2}^{s_2} S_{r_2}^{q_2} (P_{p_1 p_2, q_1 q_2} P_{r_1 r_2, s_1 s_2} - 1 - P_{p_1 p_2} P_{q_1 q_2} P_{r_1 r_2} P_{s_1 s_2}) \\
& \times \left. \int_0^\infty \hat{\Pi}_{q_2 q_3}^{p_2 p_3}(i\omega) \hat{\Pi}_{s_2 s_3}^{r_2 r_3}(i\omega) d\omega (\rho_A)_{q_1}^{p_1} (\rho_B)_{s_1}^{r_1} \right\} (p_3 q_3 | r_3 s_3)
\end{aligned} \quad (34)$$

An analogous derivation for the cumulant part leads to the expression:

$$\begin{aligned}
E_{\text{exch-disp}}^{(2)}(\mathbf{c}) = & \frac{1}{2\pi} \left\{ \int_0^\infty \hat{\Pi}_{q_1 q_3}^{p_1 p_3}(i\omega) \hat{\Lambda}_{s_1 s_2, s_3}^{r_1 r_2, r_3}(i\omega) d\omega (p_1 s_2 | v | r_1 s_1) S_{r_2}^{q_1} \right. \\
& + \int_0^\infty \hat{\Lambda}_{q_1 q_2, q_3}^{p_1 p_2, p_3}(i\omega) \hat{\Pi}_{s_1 s_3}^{r_1 r_3}(i\omega) d\omega (p_1 q_1 | v | r_1 q_2) S_{p_2}^{s_1} \\
& + (p_1 q_1 | v | r_1 s_1) S_{p_2}^{s_2} S_{r_2}^{q_2} \left[P_{p_1 p_2, q_1 q_2} \int_0^\infty \hat{\Pi}_{q_2 q_3}^{p_2 p_3}(i\omega) \hat{\Lambda}_{s_1 s_2, s_3}^{r_1 r_2, r_3}(i\omega) d\omega (\rho_A)_{q_1}^{p_1} \right. \\
& + P_{r_1 r_2, s_1 s_2} \int_0^\infty \hat{\Lambda}_{q_1 q_2, q_3}^{p_1 p_2, p_3}(i\omega) \hat{\Pi}_{s_2 s_3}^{r_2 r_3}(i\omega) d\omega (\rho_B)_{s_1}^{r_1} \\
& \left. \left. + \int_0^\infty \hat{\Lambda}_{q_1 q_2, q_3}^{p_1 p_2, p_3}(i\omega) \hat{\Lambda}_{s_1 s_2, s_3}^{r_1 r_2, r_3}(i\omega) d\omega \right] \right\} (p_3 q_3 | r_3 s_3)
\end{aligned} \quad (35)$$

In eqs 34 and 35 the summation over repeated indices is assumed (Einstein convention).

2.4. CC Exchange-Dispersion energy. The presented formalism is so far completely general, and any well-defined method for polarization propagators can be used to produce density-matrix susceptibilities for eqs 34 and 35. In particular, the energy $E_{\text{exch-disp}}^{(200)} \equiv E_{\text{exch-disp}}^{(2)}(\text{UCHF})$ can be obtained if the uncoupled HF (UCHF) propagators are used in eq 35. When the electron-correlated polarization propagators are utilized instead, the exchange-dispersion energy with the inclusion of the intramonomer correlation effect is obtained. In this work, the intramonomer correlation is studied on the CC theory level. The polarization propagators used here are obtained from time-independent CC theory developed by Moszynski et al.⁴⁹ The general equation for the imaginary-frequency CC polarization propagator from this paper adapted for our purposes takes the form:

$$\langle\langle Y; X \rangle\rangle_{i\omega}^+ = 2 \langle e^{-S} e^{T^\dagger} Y e^{-T^\dagger} e^S \Phi | \hat{\mathcal{P}} (e^{S^\dagger} \text{Re} \Omega^X(i\omega) e^{-S^\dagger}) \Phi \rangle \quad (36)$$

where Φ denotes the reference determinant, $\hat{\mathcal{P}}$ stands for the superoperator $\hat{\mathcal{P}}_1 + \hat{\mathcal{P}}_2 + \hat{\mathcal{P}}_3 + \dots$, defined in such a way that $\hat{\mathcal{P}}_n(Z)$ projects on the n -tuple excitation part of an operator Z ,⁵⁰ T is the usual amplitude operator of CC theory, and S is the excitation operator, $S = S_1 + S_2 + S_3 + \dots$, introduced in refs 9 and 50 through the formula:

$$e^S \Phi = \frac{1}{\langle e^T \Phi | e^T \Phi \rangle} e^{T^\dagger} e^T \Phi \quad (37)$$

Finally, $\Omega^X(i\omega)$ stands for the first-order perturbed operator,⁴⁹ depending linearly on the perturbation X . The time-independent theory of the CC polarization propagator has been recently implemented and studied on the CCSD level.⁵¹ Several variants of this method have been examined in ref 51 and finally the CCSD(3) model has been chosen as optimal for many-electron cases. [The CCSD(n) model includes the minimum number of terms from the expanded form of eqs 36 and 37, which is necessary to include all CCSD terms contributing on at least the $\mathcal{O}(W^m)$ order.] The CCSD(n) propagators have been already used for the induction, exchange-induction⁴² and exchange-dispersion energies³⁹ and have been shown to produce very accurate results in comparison to the benchmark values for the helium dimer.⁵² In the following, the number in parentheses will be dropped if CCSD(3) propagators are used for SAPT corrections. The experience gained from the investigation of the cumulant parts of the first-order exchange and second-order exchange-induction energies tells us that the cumulant part constitutes usually only a few percent of the total correction.^{41,42} Since the exchange-dispersion energy, unlike the exchange-induction, is small in comparison to its polarization counterpart (it usually amounts to only 5–15% of the dispersion energy in the van der Waals minimum); the cumulant part of the exchange-dispersion energy will be not implemented in the present study.

A closer examination of eq 35 reveals that the calculation of $E_{\text{exch-disp}}^{(2)}(\mathbf{n})$ scales with the sixth power of a dimension of the orbital basis N_{AO} , while in eq 35 the computational cost of the first and second terms scales with the seventh and the last term scales with the eighth power of N_{AO} . The high scaling of eq 35 is an additional argument to skip this part of the exchange-dispersion energy in practical implementations (even if programmed, it could not be used but for the smallest monomers anyway). Note parenthetically that the present formulation of the exchange-dispersion energy allows monomers to be described in different basis sets (the so-called monomer-centered basis set approach⁵³).

2.5. Density Fitting of Density-Matrix Susceptibilities. The cost of a calculation of full four-index CCSD propagators scales with the eighth power of the molecular size,³⁹ since: (i) one has to calculate $(N_{\text{AO}} + 1)N_{\text{AO}}/2$ responses to the perturbations being the $\hat{G}_q^p = 1/2(\hat{E}_q^p + \hat{E}_p^q)$ operators, where $\hat{E}_q^p = \hat{e}_{q\alpha}^{p\alpha} + \hat{e}_{\beta\beta}^{p\beta}$ are the usual orbital replacement operators^{48,54} (in this chapter

small letters will denote orbital indices); and (ii) the cost of one response calculation scales as iterative $\mathcal{O}(v^4 o^2)$, where v and o are dimensions of virtual and occupied orbital subspaces, respectively.

In ref 39 Korona and Jezierski have shown that by performing a fitting of CCSD density susceptibilities to some suitably selected auxiliary basis $\{\chi_K\}$ of a dimension N_{aux} (usually N_{aux} is only 2–3 times larger than N_{AO}), the computational cost for the CC dispersion energy can be reduced by one order of magnitude. To this end, the density susceptibility α has been expanded as

$$\alpha(\mathbf{r}_1, \mathbf{r}_2 | \omega) = - \sum_{KL} \langle \hat{\chi}_K; \hat{\chi}_L \rangle_{\omega} \chi_K(\mathbf{r}_1) \chi_L(\mathbf{r}_2) \quad (38)$$

where the operators $\hat{\chi}_K$ are defined as

$$\hat{\chi}_K = \sum_{pq} D_{pq}^K \hat{E}_q^p \quad (39)$$

with coefficients D_{pq}^K obtained from a fitting of orbital products with the auxiliary basis:

$$\phi_p(\mathbf{r}) \phi_q(\mathbf{r}) = \sum_K D_{pq}^K \chi_K(\mathbf{r}) \quad (40)$$

In the following, capital letters will be reserved for indices of the auxiliary basis set.

For the density-matrix susceptibilities it is still possible to perform a density fitting procedure on the orbital product $\phi_{p_2}(\mathbf{r}_3) \phi_{q_2}(\mathbf{r}_3)$ from eq 27 (a summation over spin is assumed to have been already performed), which leads to the following asymmetric form of α :

$$\alpha(\mathbf{r}_1 | \mathbf{r}_2; \mathbf{r}_3 | i\omega) = - \sum_{pq} \sum_K \langle \hat{E}_q^p; \hat{\chi}_K \rangle_{i\omega}^+ \phi_p(\mathbf{r}_1) \phi_q(\mathbf{r}_2) \chi_K(\mathbf{r}_3) \quad (41)$$

The expansion coefficients $\langle \hat{E}_q^p; \hat{\chi}_K \rangle_{i\omega}^+$ will be denoted as $\Pi_{qK}^p(i\omega)$. Additionally, in the next formulas a letter A and B over Π will differentiate between propagators of the monomer A and B, respectively.

After performing the summation over spins in eq 35 and making use of eq 41, the following formula is obtained for the exchange-dispersion energy with the DF approximation:

$$\begin{aligned} E_{\text{exch-disp}}^{(2)}(\mathbf{n}) = & \frac{1}{\pi} \int_0^\infty \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) d\omega (NM) (p_1 s_1 | v | r_1 q_1) \\ & + \frac{1}{2\pi} \int_0^\infty \hat{\Pi}_{q_1N}^A(i\omega) [2 \hat{\Pi}_{s_2M}^B(i\omega) d\omega (\rho_B)_{s_1}^{r_1} + 2 \hat{\Pi}_{s_1M}^B(i\omega) d\omega (\rho_B)_{s_2}^{r_2} \\ & - \hat{\Pi}_{s_1M}^B(i\omega) d\omega (\rho_B)_{s_2}^{r_1} - \hat{\Pi}_{s_2M}^B(i\omega) d\omega (\rho_B)_{s_1}^{r_2}] (NM) (p_1 s_2 | v | r_1 s_1) S_{p_2}^{q_1} \\ & + \frac{1}{2\pi} \int_0^\infty [2 \hat{\Pi}_{q_2N}^A(i\omega) (\rho_A)_{q_1}^{p_1} + 2 \hat{\Pi}_{q_1N}^A(i\omega) (\rho_A)_{q_2}^{p_2} - \hat{\Pi}_{q_1N}^A(i\omega) (\rho_A)_{q_2}^{p_1} \\ & - \hat{\Pi}_{q_2N}^A(i\omega) (\rho_A)_{q_1}^{p_2}] \hat{\Pi}_{s_1M}^B(i\omega) d\omega (NM) (p_1 q_1 | v | r_1 q_2) S_{p_2}^{s_1} \\ & + \frac{1}{4\pi} \int_0^\infty [4 \hat{\Pi}_{q_2N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) (\rho_A)_{q_1}^{p_1} (\rho_B)_{s_2}^{r_2} + 4 \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_2M}^B(i\omega) (\rho_A)_{q_2}^{p_2} (\rho_B)_{s_1}^{r_1} \\ & - 2 \hat{\Pi}_{q_2N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) (\rho_A)_{q_1}^{p_1} (\rho_B)_{s_2}^{r_1} - 2 \hat{\Pi}_{q_2N}^A(i\omega) \hat{\Pi}_{s_2M}^B(i\omega) (\rho_A)_{q_1}^{p_1} (\rho_B)_{s_1}^{r_2} \\ & - 2 \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) (\rho_A)_{q_2}^{p_2} (\rho_B)_{s_2}^{r_1} - 2 \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_2M}^B(i\omega) (\rho_A)_{q_2}^{p_2} (\rho_B)_{s_1}^{r_2} \\ & - 2 \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_2M}^B(i\omega) (\rho_A)_{q_2}^{p_1} (\rho_B)_{s_1}^{r_1} - 2 \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) (\rho_A)_{q_2}^{p_1} (\rho_B)_{s_2}^{r_2} \\ & - 2 \hat{\Pi}_{q_2N}^A(i\omega) \hat{\Pi}_{s_2M}^B(i\omega) (\rho_A)_{q_1}^{p_2} (\rho_B)_{s_1}^{r_1} - 2 \hat{\Pi}_{q_2N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) (\rho_A)_{q_1}^{p_2} (\rho_B)_{s_2}^{r_2} \\ & + \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) (\rho_A)_{q_2}^{p_1} (\rho_B)_{s_2}^{r_1} + \hat{\Pi}_{q_1N}^A(i\omega) \hat{\Pi}_{s_2M}^B(i\omega) (\rho_A)_{q_2}^{p_1} (\rho_B)_{s_1}^{r_2} \\ & \times \hat{\Pi}_{q_2N}^A(i\omega) \hat{\Pi}_{s_1M}^B(i\omega) (\rho_A)_{q_1}^{p_2} (\rho_B)_{s_2}^{r_1} + \hat{\Pi}_{q_2N}^A(i\omega) \hat{\Pi}_{s_2M}^B(i\omega) (\rho_A)_{q_1}^{p_2} (\rho_B)_{s_1}^{r_2}] d\omega (NM) (p_1 q_1 | v | r_1 s_1) S_{p_2}^{s_2} S_{r_2}^{q_2} \end{aligned} \quad (42)$$

where $(NM) = \int \chi_N(\mathbf{r}_1) r_{12}^{-1} \chi_M(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$, and the summation over spins have been performed as in ref 40. Note that the dispersion energy can also be expressed through mixed three-index propagators:

$$E_{\text{disp}}^{(2)} = - \frac{2}{\pi} \int_0^\infty \hat{\Pi}_{qN}^A(i\omega) \hat{\Pi}_{sM}^B(i\omega) d\omega (NM) (pq | rs) \quad (43)$$

It should be stressed that this equation is not bitwise compatible with the formula for the dispersion energy obtained with fully density-fitted density susceptibilities (see eq 38), but the differences should be the same order, as the accuracy of density fitting for the $(pq | rs)$ integrals (they would disappear if DF were exact). The non-DF orbital equations can be retrieved from

eq 42 by replacing auxiliary indices $N(M)$ by pairs of indices $p_3q_3(r_3s_3)$. The integral over ω is calculated numerically (for details see ref 51). In order to obtain a three-index matrix $\Pi_{qN}^p(i\omega)$, responses to N_{aux} perturbation operators $\hat{\chi}_K$ are calculated first. With $\Omega^{\hat{\chi}_K}(i\omega)$ responses in hand, a square matrix of coefficients with indices p, q running from 1 to N_{AO} can be easily obtained from eq 15 of ref 39 by inserting \hat{E}_q^p as the second perturbing operator. The computational cost of one $\Omega^{\hat{\chi}_K}(i\omega)$ operator for the CCSD case scales as $\mathcal{O}(o^2v^4)$, so for N_{aux} such operators the scaling with seventh power of the molecular size is obtained.

Note that the calculation of the exchange-dispersion energy from ready propagators is also accelerated by one order of the orbital basis size if DF is used: the calculation scales as $\mathcal{O}(N_{\text{AO}}^6)$ for the no-DF case and as $\mathcal{O}(N_{\text{AO}}^4 N_{\text{aux}})$ if DF is applied. However, this fact is of limited importance, since the calculation of the CCSD propagators is the most expensive part of the program, anyway.

The one-electron density matrices used in this paper have been obtained from CC theory for the expectation value developed by Jeziorski and Moszynski⁵⁰ and implemented on the CCSD level by Korona and Jeziorski.³⁷ The exchange-dispersion energy obtained from eq 35 with the CCSD(n) propagators⁵¹ and with XCCSD-3 density matrices³⁷ will be denoted simply as $E_{\text{exch-disp}}^{(2)}(\text{CCSD})$.

2.6. Implementation. Both DF and non-DF formulas for the noncumulant part of the exchange-dispersion energy have been implemented as a local extension of the MOLPRO code.⁵⁵ The two- and three-index Coulomb integrals, coded in MOLPRO for purposes of density fitted MP2⁵⁶ and local CCSD⁵⁷ methods, were used to obtain the $\hat{\chi}_K$ operators and to calculate the exchange-dispersion and dispersion energies from eqs 42 and 43. Since the summation over orbital indices in the CCSD half-propagator coefficients is not limited, there is no gain in performing the transformation to the molecular orbital basis in this case. Therefore, the formulas have been implemented in atomic orbitals (AO). Noteworthy, such an implementation makes it easy to extend the program to monomer-centered basis sets in the future. As already mentioned, the new code yields the $E_{\text{exch-disp}}^{(2)}(\text{UCHF})$ energy if the UCHF polarization half-propagators are inserted into eq 35. Analogously, by using the coupled HF (CHF) half-propagators, the $E_{\text{exch-disp}}^{(2)}(\text{CHF})$ energy is obtained. The calculations for the latter correction has not appeared in the literature yet, however, it has been derived and programmed in the MOLPRO code as a byproduct of SAPT(DFT) by Hessmann et al.^{27,29} The authors of these references focused however on the coupled perturbed Kohn–Sham (CKS) dispersion and exchange-dispersion energies and did not present any calculations for the CHF case. It should be stressed that in the SAPT(DFT) approach programmed in the SAPT code,^{13,31,32} the uncoupled KS (UCKS) method is used for the exchange-induction and exchange-dispersion energies, and afterward scaling formulas are applied to estimate the coupled part of these corrections, e.g., for the exchange-dispersion energy:

$$\tilde{E}_{\text{exch-disp}}^{(2)}(\text{CKS}) = \frac{E_{\text{disp}}^{(2)}(\text{CKS})}{E_{\text{disp}}^{(2)}(\text{UCKS})} E_{\text{exch-disp}}^{(2)}(\text{UCKS}) \quad (44)$$

Since the coupled variants of the interaction energy components are usually more accurate than the uncoupled ones, the SAPT(DFT) approach presented by Hessmann et al.^{27,29} should be preferred over the approach based on the UCKS method.^{31,32}

Since the new code has been programmed in the AO basis, it has been easy to examine its correctness by inserting the AO-transformed UCHF (or CHF) quantities (density-matrix susceptibilities and one-electron density matrices) instead of the CCSD ones and by checking if the obtained value is equal to the $E_{\text{exch-disp}}^{(2)}(\text{UCHF})$ (or $E_{\text{exch-disp}}^{(2)}(\text{CHF})$) energy obtained from the SAPT(DFT) program of Hessmann and Jansen.

For an efficient implementation of the exchange-dispersion energy, it is useful to define the following intermediate:

$$X_{qs}^{pr} = \frac{1}{2\pi} \int_0^\infty \tilde{\Pi}_{qN}^p(i\omega) \tilde{\Pi}_{sM}^r(i\omega) d\omega (N|M) \quad (45)$$

This quantity for fixed two indices is calculated on the fly and then used in the calculation of the corresponding part of the exchange-dispersion energy. It is possible to switch on the paging over frequencies if all three-index objects do not fit into memory. With the X_{qs}^{pr} intermediate defined, the formula given in eq 42 can be rewritten as

$$\begin{aligned} E_{\text{exch-disp}}^{(2)}(n) = & 2X_{q_1s_1}^{p_1r_1}(p_1s_1|v|r_1q_1) \\ & + [2X_{q_1s_2}^{p_1r_2}(\rho_B)_{s_1}^{r_1} + 2X_{q_1s_1}^{p_1r_2}(\rho_B)_{s_2}^{r_2} - X_{q_1s_1}^{p_1r_2}(\rho_B)_{s_1}^{r_1} - X_{q_1s_2}^{p_1r_1}(\rho_B)_{s_1}^{r_2}](p_1s_2|v|r_1s_1)S_{r_2}^{q_1} \\ & + [2X_{q_2s_1}^{p_2r_1}(\rho_A)_{q_1}^{p_1} + 2X_{q_1s_1}^{p_2r_1}(\rho_A)_{q_2}^{p_2} - X_{q_1s_1}^{p_2r_1}(\rho_A)_{q_2}^{p_1} - X_{q_2s_1}^{p_1r_1}(\rho_A)_{q_1}^{p_2}](p_1q_1|v|r_1q_2)S_{p_2}^{s_1} \\ & + \frac{1}{2}[4X_{q_2s_1}^{p_2r_1}(\rho_A)_{q_1}^{p_1}(\rho_B)_{s_2}^{r_2} + 4X_{q_1s_2}^{p_1r_2}(\rho_A)_{q_2}^{p_2}(\rho_B)_{s_1}^{r_1} \\ & - 2X_{q_2s_1}^{p_2r_2}(\rho_A)_{q_1}^{p_1}(\rho_B)_{s_2}^{r_1} - 2X_{q_2s_2}^{p_2r_1}(\rho_A)_{q_1}^{p_1}(\rho_B)_{s_1}^{r_2} - 2X_{q_1s_1}^{p_1r_2}(\rho_A)_{q_2}^{p_2}(\rho_B)_{s_2}^{r_1} \\ & - X_{q_1s_2}^{p_2r_2}(\rho_A)_{q_2}^{p_1}(\rho_B)_{s_1}^{r_1} - 2X_{q_1s_1}^{p_2r_1}(\rho_A)_{q_2}^{p_1}(\rho_B)_{s_2}^{r_2} - 2X_{q_2s_2}^{p_1r_2}(\rho_A)_{q_1}^{p_2}(\rho_B)_{s_1}^{r_1} - 2X_{q_2s_1}^{p_1r_1}(\rho_A)_{q_1}^{p_2}(\rho_B)_{s_2}^{r_2} \\ & + X_{q_1s_1}^{p_2r_2}(\rho_A)_{q_2}^{p_1}(\rho_B)_{s_2}^{r_1} + X_{q_1s_2}^{p_2r_1}(\rho_A)_{q_2}^{p_1}(\rho_B)_{s_1}^{r_2} \\ & + X_{q_2s_1}^{p_1r_2}(\rho_A)_{q_1}^{p_2}(\rho_B)_{s_2}^{r_1} + X_{q_2s_2}^{p_1r_1}(\rho_A)_{q_1}^{p_2}(\rho_B)_{s_1}^{r_2}](p_1q_1|v|r_1s_1)S_{p_2}^{s_2}S_{r_2}^{q_2} \end{aligned} \quad (46)$$

A ready-to-program version of eq 46 is presented in the Appendix Section.

Equation 46 resembles closely the UCHF formula for the exchange-dispersion energy.⁷ In particular, the intermediate X is an analog of the mixed double amplitude from ref 7. This correspondence is examined in detail for one selected term in the Appendix Section.

It should be noted that an intermediate similar to X_{rs}^{pq} appears in the implementation of DF-DFT-SAPT,²⁹ where it is also constructed from three-index objects (partially density-fitted CKS half-propagators). It should be stressed, however, that the present approach derives rigorously the general expression of the exchange-dispersion energy in a form of density-matrix susceptibilities and density matrices, while in ref 29 a theoretical background of a replacement of the UCHF quantities by CKS or CHF ones has not been presented.

3. Results and Discussion

3.1. Computational Details. To illustrate the performance of the method presented in the previous sections several test calculations have been performed.

At the beginning the quality of DF for the exchange-dispersion energy has been investigated for the van der Waals complex of two neon atoms. In this test the distances between atoms range from 3 to 9 bohr, thus covering repulsive, minimum, and long-range regions of PES. The augmented correlation-consistent aug-cc-pVDZ^{58–60} basis has been used in this case because of the necessity of performing the calculations without the density fitting approximation (scaling with the eighth power of the molecular size). The auxiliary basis sets proposed in refs 61 and 62 were utilized. The basis sets optimized for the MP2 correlation energy will be denoted as aug-cc-pVXZ/MP2fit ($X = D, T, Q$), while other basis sets optimized for the Coulomb and exchange integrals will be denoted as cc-pVXZ/JKfit. The DF calculations for a larger aug-cc-pVTZ orbital basis have been also performed.

The new approach has been then applied to the helium dimer at various distances used previously to produce an accurate PES for this van der Waals complex.^{52,63} The same basis set (DC147) as in refs 52 and 63 has been used. A large auxiliary basis (aug-cc-pVQZ/MP2fit)^{61,62} augmented with the functions on the midbond (see ref 39 for details) has served for a density fitting in this case. Additionally, for the $r = 5.6$ bohr a smaller DC77 basis from ref 52 has been used to calculate the exchange-dispersion energy without density fitting. The numerical quadrature with 20 integration points has been applied for the neon and helium dimers in order to eliminate uncertainties related to the quality of the numerical integration when comparing no-DF and DF energies.

Finally, the new approach has been used to calculate the exchange-dispersion and dispersion energies for selected noncovalent complexes at geometries close to global minima. These complexes are representative to various types of dominant interactions at minimum, ranging from polar systems to dispersion-bound species. The selected complexes, along with the geometry references, are the following: $(\text{H}_2\text{O})_2$,⁷ $(\text{HF})_2$,⁷ $(\text{N}_2)_2$,⁶⁴ $(\text{CO})_2$,⁶⁵ $\text{CO}-\text{H}_2\text{O}$,^{38,66} Ar_2 ,³¹ $\text{He}-\text{HF}$, and $\text{Ne}-\text{Ar}$. For the $\text{Ne}-\text{Ar}$ complex, a distance of 3.65 Å between atoms has been used. For the $\text{He}-\text{HF}$ complex a distance between the helium atom and the center of mass of the HF molecule ($R_{\text{H-F}} = 1.7328$ bohr) has been set to 6.5 bohr. Some of these complexes have been previously used to study the intramonomer correlation effects for the induction³⁸ and dispersion³⁹ energies. For all cases,

the aug-cc-pVTZ orbital basis and the corresponding aug-cc-pVTZ/MP2fit basis sets have been used. The 8-point numerical quadrature has been utilized.

The core electrons (1s for C, N, O, F, and Ne and 1s2s2p for Ar) have been frozen in the CC calculations. All results have been produced with a local development version of the MOLPRO suite of codes. The SAPT(DFT) results have been obtained by using the PBE0 functional^{67,68} with the asymptotic correction of Grüning et al.⁶⁹ and utilizing the code available in MOLPRO and developed by Hesselmann and Jansen.^{24–27} The ionization potentials needed for the calculation of the asymptotic corrections have been obtained from ref 70.

3.2. Discussion of the Results. Since the calculation of the CCSD density-matrix susceptibility without density fitting scales with the eighth power of the molecular size, the possibility of obtaining a good quality DF-CCSD exchange-dispersion energies is crucial for the range of the applicability of the new method. Therefore, it is important to examine errors introduced by the DF approximation. Table 2 presents the dispersion and exchange-dispersion energies for the Ne_2 complex calculated from CCSD(3) propagators, obtained either without DF or with DF for various auxiliary basis sets. In the table, the DF results are followed by the percent errors with respect to the exact (non-DF) value. It can be seen from Table 2 that the dispersion energy is not very sensitive to a quality of auxiliary basis sets. All basis sets (even cc-pVTZ/JKfit) produce results of a similar quality with errors on the fourth digit in a majority of cases. [Note parenthetically that the dispersion energies presented here were obtained from eq 43, so they are not bitwise compatible with values from ref 39 calculated from two-index propagators.] The exchange-dispersion energy is, however, more sensitive to the quality of auxiliary basis sets, especially for large distances. From the results presented in Table 2, it can be seen that acceptable errors of a couple percent for the whole range of distances are produced by the aug-cc-pVXZ/MP2fit, $X = T, Q$ basis sets only. In view of rather substantial errors of the DF exchange-dispersion for the largest distances considered, it is interesting to examine the total error introduced by DF for the sum of the dispersion and exchange-dispersion energies. The corresponding errors for the aug-cc-pVDZ/MP2fit basis set are presented in the last line of the results for the aug-cc-pVDZ orbital basis. It turns out that errors of the exchange-dispersion energy at the large- R region are not important since contributions from the exchange-dispersion energy in this region are negligible anyway. On the other hand, for the repulsive-wall region the error caused by density fitting applied to $E_{\text{exch-disp}}^{(2)}$

Table 2. Dispersion and Exchange-Dispersion Energies for Two Neon Atoms (Upper Numbers) Computed from Density-Fitted CCSD(3) Density-Matrix Susceptibilities and Their Percentage Errors^a

basis set	distance						
	3.0	4.0	5.0	6.0	7.0	8.0	9.0
aug-cc-pVDZ							
	$E_{\text{disp}}^{(2)}$						
no-DF	-11.645	-2.2700	-0.4732	-0.13178	-0.04750	-0.020144	-0.009601
aug-cc-pVDZ/MP2fit	-11.649	-2.2702	-0.4731	-0.13176	-0.04749	-0.020139	-0.009601
	-0.032	-0.0094	0.013	0.010	0.0082	0.021	0.0085
aug-cc-pVTZ/MP2fit	-11.645	-2.2699	-0.4732	-0.13165	-0.04749	-0.020141	-0.009599
	0.0065	0.0043	-0.0032	0.093	0.010	0.012	0.029
aug-cc-pVQZ/MP2fit	-11.644	-2.2698	-0.4732	-0.13178	-0.04750	-0.020147	-0.009603
	0.0077	0.0087	-0.0035	-0.0046	-0.0086	-0.017	-0.017
cc-pVTZ/JKfit	-11.638	-2.2663	-0.4732	-0.13188	-0.04752	-0.020141	-0.009596
	0.060	0.16	-0.0007	-0.080	-0.049	0.011	0.056
cc-pVQZ/JKfit	-11.640	-2.2681	-0.4733	-0.13189	-0.04752	-0.020142	-0.0095963
	0.045	0.081	-0.024	-0.088	-0.057	0.0070	0.053
	$E_{\text{exch-disp}}^{(2)}$						
no-DF	4.619	0.5582	0.05271	0.004531	0.000445	0.0000448	0.00000549
aug-cc-pVDZ/MP2fit	4.610	0.5559	0.05256	0.004511	0.000436	0.0000411	0.00000452
	0.20	0.41	0.29	0.43	2.14	8.09	18.
aug-cc-pVTZ/MP2fit	4.616	0.5573	0.05265	0.004608	0.000453	0.0000458	0.00000588
	0.067	0.16	0.11	-1.71	-1.78	-2.29	-7.04
aug-cc-pVQZ/MP2fit	4.618	0.5578	0.05266	0.004525	0.000443	0.0000442	0.00000539
	0.023	0.079	0.088	0.13	0.37	1.29	1.84
cc-pVTZ/JKfit	4.604	0.5528	0.05222	0.004368	0.000387	0.0000286	0.00000194
	0.32	0.96	0.94	3.59	13.	36.	65.
cc-pVQZ/JKfit	4.612	0.5557	0.05239	0.004383	0.000389	0.0000287	0.00000194
	0.16	0.44	0.60	3.26	13.	36.	65.
	percent error of $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$						
aug-cc-pVDZ/MP2fit	-0.18	-0.14	-0.021	-0.0044	-0.012	0.0025	-0.0016
aug-cc-pVTZ							
	$E_{\text{disp}}^{(2)}$						
aug-cc-pVDZ/MP2fit	-15.228	-2.915	-0.6669	-0.18267	-0.06388	-0.026839	-0.012734
aug-cc-pVTZ/MP2fit	-15.298	-2.924	-0.6640	-0.18290	-0.06390	-0.026838	-0.012735
aug-cc-pVQZ/MP2fit	-15.300	-2.924	-0.6642	-0.18298	-0.06392	-0.026845	-0.012739
cc-pVTZ/JKfit	-15.286	-2.918	-0.6627	-0.18279	-0.06386	-0.026820	-0.012726
	$E_{\text{exch-disp}}^{(2)}$						
aug-cc-pVDZ/MP2fit	5.35	0.643	0.0707	0.00679	0.00059	0.000055	0.0000055
aug-cc-pVTZ/MP2fit	5.43	0.655	0.0721	0.00701	0.00061	0.000059	0.0000062
aug-cc-pVQZ/MP2fit	5.44	0.656	0.0724	0.00699	0.00061	0.000060	0.0000064
cc-pVTZ/JKfit	5.39	0.642	0.0699	0.00658	0.00053	0.000043	0.0000032

^a Lower numbers, for the smaller orbital basis only, relative to the results obtained without density fitting (denoted as no-DF). Energies are in millihartrees, distances are in bohr.

determines the total error of the sum of the dispersion and exchange-dispersion energies. However, differences between the DF and no-DF results of order of a few tenths of percent are acceptable in most applications. It can be, therefore, recommended that for the aug-cc-pVXZ basis set just the corresponding MP2fit auxiliary basis can be safely used for the SAPT(CCSD) calculations, unless we are specifically interested in the exchange-dispersion energy (for the latter case the aug-cc-pVQZ/MP2fit auxiliary basis should be utilized).

In Table 2 the DF-CCSD dispersion and exchange-dispersion energies for a larger aug-cc-pVTZ orbital basis are also presented. The results show that the exchange-dispersion energies calculated with the aug-cc-pVDZ/MP2fit and aug-cc-pVTZ/MP2fit basis sets do not differ much from each other, therefore the smaller auxiliary basis can also be used with this orbital basis.

The DF-CCSD exchange-dispersion energy for the helium dimer is shown in Table 3. The full configuration interaction (FCI) exchange-dispersion energies within the S^2 approxima-

tion listed in this table are the unpublished results collected during the calculations performed to obtain the PES for the interaction of two helium atoms.^{52,63} The CCSD(4) propagators have been utilized in this case,⁵¹ which are practically exact (equivalent to FCI) for two-electron monomers (actually, it has been checked out that the results obtained with the CCSD(3) and CCSD(4) models differ by less than 0.1% for all values listed in the table). As discussed in ref 51, that differences between the DF-CCSD and FCI dispersion energies can be attributed exclusively to the DF error. However, for the case of the density-fitted exchange-dispersion energy two sources of errors are possible: one stemming from density fitting and the second one related to the neglect of the cumulant contribution (see eq 35). The experience gained from the investigation of the Ne₂ complex tells us that the DF errors can be of order of 1–2% percent in the minimum region. Therefore, large differences between the $E_{\text{exch-disp}}^{(2)}$ (CCSD) and $E_{\text{exch-disp}}^{(2)}$ (FCI) corrections for distances from 3.0 to 4.0 bohr (corresponding to a highly repulsive region of PES) should be attributed rather to the cumulant

Table 3. Second-Order Exchange-Dispersion Energies in Various Approximations for the Helium Dimer^a

method	R								
	3.0	3.5	4.0	4.5	5.0	5.3	5.6	6.0	7.0
FCI	627.6	212.7	73.06	24.98	8.453	4.386	2.265	0.9316	0.09718
DF-CCSD(4)	479	191	70.5	25.0	8.59	4.47	2.31	0.950	0.0975
	−24	−10	−3.5	−0.14	1.6	2.0	2.1	1.9	0.4
UCHF	349.3	139.7	51.29	17.93	6.075	3.139	1.611	0.6557	0.06637
	−44	−34	−29	−28	−28	−28	−29	−30	−32
CHF	423.4	171.2	63.59	22.50	7.710	4.008	2.068	0.8476	0.08691
	−33	−20	−13	−10	−8.8	−8.6	−8.7	−9.0	−11
UCKS	431	179	67.1	23.8	8.15	4.22	2.17	0.882	0.0886
	−31	−16	−8.1	−4.6	−3.6	−3.8	−4.3	−5.3	−8.8
'scaled UCKS'	415	174	65.8	23.4	8.01	4.14	2.13	0.863	0.0862
	−34	−18	−10	−6.2	−5.3	−5.5	−6.2	−7.3	−11
CKS	467	192	72.4	25.8	8.86	4.60	2.37	0.965	0.0974
	−25	−9.6	−0.9	3.3	4.8	4.8	4.5	3.7	0.2

^a The second rows contain the percent errors with respect to the FCI exchange-dispersion energy (in the S^2 approximation). Energies are in μ hartrees, distances are in bohr.

part of the exchange-dispersion energy. For larger distances, the differences are smaller than 2%, so they are of the same order of magnitude as some DF errors in Table 2, and it is difficult to attribute them unanimously to DF or cumulant sources of error. In order to clarify this point a non-DF calculation has been performed for a distance 5.6 bohr in a smaller DC77 basis, giving the value of the (noncumulant) CCSD exchange-dispersion energy (eq 35) equal to 2.2867 μ hartree. For this distance, the $E_{\text{exch-disp}}^{(2)}(\text{FCI})$ energy in the S^2 approximation (2.2279 μ hartree) is available from unpublished calculations, utilizing a SAPT program specific for two-electron monomers used also in refs 52, 63, and 71. A subtraction of these two numbers gives, therefore, a pure cumulant term for the helium dimer (eq 35). It turns out that for the van der Waals minimum region this contribution constitutes −2.6% of a total FCI exchange-dispersion energy, i.e., is small enough to be neglected (this difference is only 0.2% of the total interaction energy). Summarizing, the cumulant contribution for the helium dimer is significant only in highly repulsive regions of PES (where it contributes by ca. 25% to the total exchange-dispersion energy for He_2 , see Table 3), while in all other regions this term is hidden within uncertainties caused by the DF approximation. Unfortunately, for many-electron monomers there is no reliable benchmark for the exchange-dispersion energy, so the issue of the importance of the cumulant contribution cannot be solved unambiguously at the moment. However, it is known for previous calculations that similar cumulant contributions for the first-order exchange⁴⁰ and second-order exchange-induction⁴² energies contribute an unsubstantial fraction to the total energy correction. It can be, therefore, anticipated that the cumulant part of the exchange-dispersion energy should be small as well. It should be also noted that the calculation of the cumulant contribution for many-electron monomers would be very expensive, since six-index (five-index with DF) objects should have been stored for a number of frequencies on the one hand, and the numerical quadrature itself would scale with the eighth (seventh with DF) power of the molecular size on the other.

In Table 3 the UCHF, CHF and DFT exchange-dispersion energies for the helium dimer are also listed for a comparison. As it can be seen from this table, the errors of about 30% are common for the $E_{\text{exch-disp}}^{(2)}(\text{UCHF})$ energy. Errors become

about three times smaller if the CHF polarization propagators are used instead of the UCHF ones. On the other side, the exchange-dispersion energies obtained from the asymptotically corrected PBE0 functional and CKS propagators show similar errors relative to the $E_{\text{exch-disp}}^{(2)}(\text{FCI})$ exact values as the $E_{\text{exch-disp}}^{(2)}(\text{CCSD})$ results. Therefore, the conclusions can be made that the CKS propagators for helium reproduce rather well the exact propagators, if the asymptotically corrected PBE0 functional is used. On the other hand, the quality of the UCKS exchange-dispersion energies with the same functional is significantly worse. It should be stressed that the usage of the scaling formula (44) deteriorates the agreement with the FCI benchmark values in comparison to the unscaled UCKS energies for all distances considered.

In Table 4 the dispersion and exchange-dispersion energies for several van der Waals complexes are listed. These energies have been calculated with DF-CCSD, UCHF, CHF, and DFT approaches for monomers. A comparison of the results listed in Table 4 with the DF-CCSD values, serving as the benchmark, supports the conclusion reached for the helium dimer that the UCHF method underestimates substantially the exchange-dispersion energy (by even 38% for the He-HF complex). Unfortunately, the CHF approach does not help to the same extent, as in the case of He_2 , although errors of the CHF corrections do become somewhat smaller.

Finally, let us examine the DFT exchange-dispersion energies. Again, three values of this correction listed in the table correspond to the UCKS, 'scaled UCKS' (see eq 44), and true CKS methods. It can be observed that the CKS results are remarkably close to the benchmark values in all cases, while errors in the UCKS and 'scaled UCKS' methods are much larger (with one exception of the Ne-Ar complex, for which the UCKS exchange-dispersion energy is close to the DF-CCSD benchmark). In particular, the 'scaled UCKS' approach does not represent any improvement over the UCKS approach, since usually the 'scaled UCKS' exchange-dispersion energy 'overshoots' the DF-CCSD value from the other side, although the errors are somewhat smaller in some cases. Summarizing, from three SAPT(DFT) approaches for a calculation of the exchange-dispersion only the method utilizing the CKS propagators can be recommended. If the CKS propagators are unavailable, one should rather use

Table 4. A Comparison of the Exchange-Dispersion Energies Computed with the DF-CCSD(3), UCHF, CHF, and UCKS, 'Scaled UCKS', and CKS Approaches for Monomers^a

method	complex							
	Ne–Ar	Ar ₂	(H ₂ O) ₂	(HF) ₂	(CO) ₂	(N ₂) ₂	CO–H ₂ O	He–HF
				$E_{\text{exch-disp}}^{(2)}$				
DF-CCSD	0.0114	0.061	0.642	0.527	0.092	0.045	0.083	0.0053
UCHF	0.0085	0.055	0.495	0.381	0.064	0.029	0.059	0.0033
CHF	0.0093	0.059	0.527	0.400	0.072	0.035	0.063	0.0040
UCKS	0.0111	0.075	0.733	0.587	0.104	0.050	0.102	0.0051
'scaled UCKS'	0.0085	0.050	0.575	0.481	0.070	0.040	0.071	0.0045
CKS	0.0101	0.063	0.628	0.513	0.092	0.047	0.084	0.0054
				$E_{\text{disp}}^{(2)}$				
DF-CCSD	−0.267	−0.846	−3.651	−3.176	−1.048	−0.537	−1.013	−0.1663
UCHF	−0.244	−0.918	−3.116	−2.556	−0.967	−0.449	−0.910	−0.1261
CHF	−0.236	−0.815	−3.200	−2.673	−0.931	−0.477	−0.873	−0.1443
UCKS	−0.329	−1.270	−4.511	−3.758	−1.499	−0.662	−1.400	−0.1874
CKS	−0.253	−0.852	−3.543	−3.079	−1.016	−0.539	−0.976	−0.1650

^a Dispersion energies are also listed for a comparison. Energies are in millihartrees.

UCKS propagators without trying to improve them by introducing some provisional scaling procedures.

4. Summary

A new formulation of the second-order exchange-dispersion energy in the single-exchange approximation has been presented. The exchange-dispersion energy is expressed through the formula involving frequency-dependent density-matrix susceptibilities and one-electron density matrices of monomers, in the spirit of the Longuet-Higgins formula for the second-order dispersion energy. An explicit cancellation of disconnected terms has been achieved through the introduction of the cumulant density susceptibilities. The new approach has been applied to the case of the CCSD polarization propagators for the main (noncumulant) part of the exchange-dispersion energy. In this way the exchange-dispersion energy with the inclusion of the intramonomer correlation effects has been obtained for the first time for many-electron systems. The density fitting technique has been applied to density-matrix susceptibilities in order to reduce the computational time. For the CCSD susceptibilities,

the CPU time has been scaled down in this way from the eighth to seventh power in terms of the orbital basis size, thus allowing to perform benchmark calculations for a few-atom monomers. The relative error of density fitting for the case of the exchange-dispersion energy is somewhat larger than for the dispersion energy and sometimes constitutes a couple percent of the whole correction in the minimum and even about 10% or more for large distances. However, since the exchange-dispersion energy is usually much smaller than the dispersion energy, the error resulted from density fitting with respect to the sum of exchange-dispersion and dispersion energies is of order of a few tenths of percent. A comparison with benchmark DF-CCSD values has allowed to assess the quality of the three common SAPT(DFT) approaches for the calculation of the exchange-dispersion energy. It turns out that the CKS exchange-dispersion energy is usually in a very good agreement with DF-CCSD, while the quality of the UCKS energies is significantly worse in a majority of cases. Finally, the numerical investigation of the 'scaled UCKS' approach shows that this method should be abandoned in favor to the CKS exchange-dispersion energy.

5. Appendix

5.1. The Exchange-Induction Energy Expressed through Density-Matrix Susceptibilities. A computationally efficient way to express the second-order exchange-induction energy through monomer properties has been developed in ref 42 where the ground-state and first-order density matrices have been used for this purpose (with the effective electrostatic potential of the second monomer acting as a perturbing operator). From a theoretical point of view, it may be interesting to express this correction analogously to the induction energy, for which the following formula exists in the literature:^{72,73}

$$E_{\text{ind}}^{(2)}(\text{A} \leftarrow \text{B}) = -\frac{1}{2} \int v_{\text{eff,B}}(1) \alpha_{\text{A}}(1, 1'|0) v_{\text{eff,B}}(1') d\tau_1 d\tau_1' \quad (47)$$

In eq 47, the effective electrostatic potential of the monomer B is used, which is defined as

$$v_{\text{eff,B}}(1) = v_{\text{B}}(1) + \int \frac{\rho_{\text{B}}(1'1')}{r_{11'}} d\tau_1' \quad (48)$$

where in turn v_{B} is the one-electron potential of the monomer B. The formula for the $E_{\text{ind}}^{(2)}(\text{B} \leftarrow \text{A})$ term is completely analogous. Repeating derivation steps shown in the first part of this paper, the exchange-induction energy in the S^2 approximation can be written in terms of the static density-matrix susceptibilities:

$$\begin{aligned}
E_{\text{exch-ind}}^{(2)}(\mathbf{A} \leftarrow \mathbf{B}) = & \frac{1}{2} \int v(1, 1') v_{\text{eff,B}}(3) \alpha_{\mathbf{A}}(1|1'; 3|0) \rho_{\mathbf{B}}(1'1) d\tau_1 d\tau'_1 d\tau_3 \\
& + \frac{1}{2} \int v(1, 1') v_{\text{eff,B}}(3) \alpha_{\mathbf{A}}(1|2'; 3|0) \mathcal{L}_{1'2'}^{\mathbf{B}} \rho_{\mathbf{B}}(1'1|1') \rho_{\mathbf{B}}(2'1) d\tau_1 d\tau'_1 d\tau'_2 d\tau_3 \\
& + \frac{1}{2} \int v(1, 1') v_{\text{eff,B}}(3) \mathcal{L}_{12}^{*\mathbf{A}} \mathcal{L}_{1'2'}^{\mathbf{A}} \alpha_{\mathbf{A}}(1|1; 3|0) \rho_{\mathbf{A}}(2|1') \rho_{\mathbf{B}}(1'1|2) d\tau_1 d\tau'_1 d\tau_2 d\tau_3 \\
& + \frac{1}{2} \int v(1, 1') v_{\text{eff,B}}(3) \\
& \times [(\mathcal{L}_{12}^{*\mathbf{A}} \mathcal{L}_{12'}^{\mathbf{A}} \mathcal{L}_{1'2'}^{\mathbf{B}} - 1 - \pi_{12}^{*\mathbf{A}} \pi_{1'2'}^{\mathbf{A}}) \alpha_{\mathbf{A}}(1|1; 3|0) \rho_{\mathbf{A}}(2|2') \rho_{\mathbf{B}}(1'1|1') \rho_{\mathbf{B}}(2'1|2) \\
& + \alpha_{\mathbf{A}}(1|2'; 3|0) \Lambda_{\mathbf{B}}(1'2'1|2) + \lambda_{\mathbf{A}}(12|12'; 3|0) \rho_{\mathbf{B}}(1'1|2) \\
& + \mathcal{L}_{12}^{*\mathbf{A}} \mathcal{L}_{1'2'}^{\mathbf{A}} \alpha_{\mathbf{A}}(1|1; 3|0) \rho_{\mathbf{A}}(2|2') \Lambda_{\mathbf{B}}(1'2'1|2) \\
& + \lambda_{\mathbf{A}}(12|12'; 3|0) \mathcal{L}_{1'2'}^{\mathbf{B}} \rho_{\mathbf{B}}(1'1|1') \rho_{\mathbf{B}}(2'1|2) + \lambda_{\mathbf{A}}(12|12'; 3|0) \Lambda_{\mathbf{B}}(1'2'1|2)] d\tau_1 d\tau'_1 d\tau_2 d\tau'_2 d\tau_3
\end{aligned} \quad (49)$$

where $\Lambda_{\mathbf{B}}(12|1'2')$ denotes the two-electron density-matrix cumulant⁷⁴ of the monomer B, which for the CC case has been derived in ref 41. The first four terms inside the square brackets correspond to the noncumulant part of the exchange-induction energy. Equation 49 is interesting from a formal point of view, since it expresses the exchange-induction energy through quantities independent of another monomer. The calculation of this correction by using eq 49 would require a knowledge of the whole density-matrix susceptibility. Clearly, from the computational point of view, it is more convenient to calculate one response of the monomer with respect to the potential of another monomer and to use the resulting first-order density matrix for the calculation of the exchange-induction energy, than to calculate ca. N_{AO}^2 or N_{aux} responses to the \hat{G}_q^p or $\hat{\chi}_K$ operators. However, eq 49 could be in principle an interesting alternative to the approach presented in ref 42 if it were sufficient to obtain monomer properties for SAPT in a purely monomer basis set.

5.2. Working Formula for the Exchange-Dispersion Energy. An implementation of eq 35 can be further simplified if one utilizes the generalized Coulomb and exchange matrices, introduced in ref 39. In the formula below the capital bold letters denote a matrix of $N_{\text{AO}} \times N_{\text{AO}}$ dimensions, the one-electron density matrices of monomers are denoted by the capital bold letters \mathbf{A} and \mathbf{B} , while \mathbf{S} stands for the overlap matrix. The definitions of *generalized* right and left Coulomb matrices and *generalized* inner and outer exchange matrices for a general (not necessarily symmetric) matrix \mathbf{Y} are listed below:

$$\begin{aligned}
\mathbf{J}(\mathbf{Y})_r^s &= Y_{s'}^r(rs|v|r's') \\
\mathbf{J}(\mathbf{Y})_{r'}^{s'} &= Y_s^r(rs|v|r's') \\
\mathbf{K}(\mathbf{Y})_r^{s'} &= Y_s^r(rs|v|r's') \\
\mathbf{K}(\mathbf{Y})_{r'}^s &= Y_s^r(rs|v|r's')
\end{aligned} \quad (50)$$

With these definitions the exchange-dispersion energy can be expressed as

$$\begin{aligned}
E_{\text{exch-disp}}^{(2)}(\mathbf{n}) = & 2X_{q_1s_1}^{p_1r_1}(p_1s_1|v|r_1q_1) \\
& + 2X_{q_1s_2}^{p_1r_2}\mathbf{S}_{r_2}^{q_1}\mathbf{J}(\mathbf{B})_{p_1}^{s_2} + 2X_{q_1s_1}^{p_1r_1}(\mathbf{S}\mathbf{B})_{s_2}^{q_1}(p_1s_2|v|r_1s_1) - X_{q_1s_1}^{p_1r_2}\mathbf{S}_{r_2}^{q_1}\mathbf{K}(\mathbf{B})_{p_1}^{s_1} \\
& - X_{q_1s_2}^{p_1r_1}(\mathbf{S}\mathbf{B})_{s_1}^{q_1}(p_1s_2|v|r_1s_1) \\
& + \left[2X_{q_2s_1}^{p_2r_1}\mathbf{J}(\mathbf{A})_{r_1}^{q_2}\mathbf{S}_{p_2}^{s_1} + 2X_{q_1s_1}^{p_1r_1}(\mathbf{S}\mathbf{A})_{q_2}^{s_1}(p_1q_1|v|r_1q_2) - X_{q_1s_1}^{p_2r_1}\mathbf{K}(\mathbf{A})_{r_1}^{q_1}\mathbf{S}_{p_2}^{s_1} \right] \\
& - X_{q_2s_1}^{p_1r_1}(\mathbf{S}\mathbf{A})_{q_1}^{s_1}(p_1q_1|v|r_1q_2) \\
& + \frac{1}{2} \left[4X_{q_2s_1}^{p_2r_1}(\mathbf{S}\mathbf{B}\mathbf{S})_{p_2}^{q_2}\mathbf{J}(\mathbf{A})_{r_1}^{s_1} + 4X_{q_1s_2}^{p_1r_2}(\mathbf{S}\mathbf{A}\mathbf{S})_{q_2}^{s_2}\mathbf{J}(\mathbf{B})_{p_1}^{q_1} \right. \\
& - 2X_{q_2s_1}^{p_2r_2}\mathbf{S}_{r_2}^{q_2}\mathbf{J}(\mathbf{A})_{r_1}^{s_1}(\mathbf{B}\mathbf{S})_{p_2}^{r_1} - 2X_{q_2s_2}^{p_2r_1}\mathbf{S}_{p_2}^{s_2}(\mathbf{S}\mathbf{B})_{s_1}^{q_2}\mathbf{J}(\mathbf{A})_{r_1}^{s_1} \\
& - 2X_{q_1s_1}^{p_1r_2}(\mathbf{B}\mathbf{S}\mathbf{A}\mathbf{S})_{r_2}^{q_1}(p_1q_1|v|r_1s_1) - 2X_{q_1s_2}^{p_1r_1}(\mathbf{S}\mathbf{A}\mathbf{S}\mathbf{B})_{s_1}^{q_1}(p_1q_1|v|r_1s_1) \\
& - 2X_{q_1s_2}^{p_2r_2}\mathbf{S}_{p_2}^{s_2}\mathbf{J}(\mathbf{B})_{p_1}^{q_1}(\mathbf{A}\mathbf{S})_{r_2}^{p_1} - 2X_{q_1s_1}^{p_2r_1}(\mathbf{A}\mathbf{S}\mathbf{B}\mathbf{S})_{p_2}^{p_1}(p_1q_1|v|r_1s_1) \\
& - 2X_{q_2s_2}^{p_1r_2}(\mathbf{S}\mathbf{A})_{q_1}^{s_2}\mathbf{J}(\mathbf{B})_{p_1}^{q_1}\mathbf{S}_{r_2}^{q_2} - 2X_{q_2s_1}^{p_1r_1}(\mathbf{S}\mathbf{B}\mathbf{S}\mathbf{A})_{q_1}^{q_2}(p_1q_1|v|r_1s_1) \\
& + X_{q_1s_1}^{p_2r_2}(\mathbf{A}\mathbf{S})_{r_2}^{p_1}(\mathbf{B}\mathbf{S})_{p_2}^{r_1}(p_1q_1|v|r_1s_1) + X_{q_1s_2}^{p_2r_1}\mathbf{K}(\mathbf{A}\mathbf{S}\mathbf{B})_{r_1}^{q_1}\mathbf{S}_{p_2}^{s_2} \\
& \left. + X_{q_2s_1}^{p_1r_2}\mathbf{S}_{r_2}^{q_2}\mathbf{K}(\mathbf{B}\mathbf{S}\mathbf{A})_{p_1}^{s_1} + X_{q_2s_2}^{p_1r_1}(\mathbf{S}\mathbf{B})_{q_1}^{q_2}(\mathbf{S}\mathbf{A})_{q_1}^{s_2}(p_1q_1|v|r_1s_1) \right]
\end{aligned} \quad (51)$$

The quantities like products of the overlap and density matrices or the generalized Coulomb and exchange matrices can be calculated in advance and stored on disk. Unfortunately, not all terms can be factorized in this way, so still the overall scaling of eq 51 remains (N_{AO}^3), although with a lower prefactor. As already noted, the scaling of eq 51 is of a limited importance in view of high costs of the DF-CCSD propagators.

5.3. A Comparison with the Formula for the UCHF Exchange-Dispersion Energy. In order to find a correspondence between the new formula (eq 35) and the UCHF exchange-dispersion energy (eq 108 of ref 7) let us consider the first term of eq 35, in which the UCHF propagators have been used. If Ψ^0 is set to Φ (Hartree–Fock determinant) and Ψ^K are approximated by singly-excited determinants $\Psi^K = \Phi(i \rightarrow a)$, then the propagator formula (see eq 28) takes the form:

$$\begin{aligned}\Pi_{q_1 q_2}^{p_1 p_2}(i\omega) &= 2 \sum_{ia} \langle \Phi | \mathcal{E}_{q_1}^{p_1} \Phi(i \rightarrow a) \rangle \langle \Phi(i \rightarrow a) | \mathcal{E}_{q_2}^{p_2} \Phi \rangle \frac{\Delta_{ai}}{(\Delta_{ai})^2 + \omega^2} \\ &= 2 \sum_{ia} \delta_i^{p_1} \delta_{q_1}^a \delta_a^{p_2} \delta_{q_2}^i \frac{\Delta_{ai}}{(\Delta_{ai})^2 + \omega^2}\end{aligned}\quad (52)$$

where $\Delta_{ai} = \varepsilon_a - \varepsilon_i$ is a difference of orbital energies for spinorbitals ϕ_a and ϕ_i (a, b and i, j denote virtual and occupied indices, respectively, relative to Φ). If eq 52 is inserted into the first term of eq 35, then the following expression is obtained

$$\begin{aligned}&\frac{1}{2\pi} \int_0^\infty \Pi_{q_1 q_2}^{p_1 p_2}(i\omega) \Pi_{s_1 s_2}^{r_1 r_2}(i\omega) d\omega (p_1 s_1 | v | r_1 q_1) (p_2 q_2 | r_2 s_2) \\ &= \sum_{ia \in A} \sum_{jb \in B} \frac{2}{\pi} \int_0^\infty \frac{\Delta_{ai}}{(\Delta_{ai})^2 + \omega^2} \frac{\Delta_{bj}}{(\Delta_{bj})^2 + \omega^2} d\omega (ib | v | ja) (ailbj) \\ &= \sum_{ia \in A} \sum_{jb \in B} \frac{1}{\Delta_{ai} + \Delta_{bj}} (ailbj) (ib | v | ja) = -t_{ab}^{ij} (ib | v | ja)\end{aligned}\quad (53)$$

which, after the summation over spins, gives the first term of eq 108 in ref 7. Note that this paper contains several misprints corrected recently in ref 75.

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References

- (1) Jeziorski, B.; Moszynski, R.; Szalewicz, K. *Chem. Rev.* **1994**, *94*, 1887.
- (2) Szalewicz, K.; Jeziorski, B. Symmetry-Adapted Perturbation Theory of Intermolecular Interactions. In *Molecular Interactions—from van der Waals to Strongly Bound Complexes*; Schreiner, S., Ed.; Wiley: New York, 1997; pp 3–43.
- (3) Szalewicz, K.; Patkowski, K.; Jeziorski, B. *Struct. Bonding (Berlin)* **2005**, *116*, 43.
- (4) Moszynski, R.; Jeziorski, B.; Ratkiewicz, A.; Rybak, S. *J. Chem. Phys.* **1993**, *99*, 8856.
- (5) Szalewicz, K.; Jeziorski, B. *Mol. Phys.* **1979**, *38*, 191.
- (6) Jeziorski, B.; Moszynski, R.; Rybak, S.; Szalewicz, K. Many-Body Theory of van der Waals Interactions. In *Many-Body Methods in Quantum Chemistry*; Kaldor, U., Ed.; Springer: New York, 1989; Vol. 52 of *Lecture Notes in Chemistry*; pp 65–94.
- (7) Rybak, S.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1991**, *95*, 6576.
- (8) Moszynski, R.; Jeziorski, B.; Szalewicz, K. *Int. J. Quantum Chem.* **1993**, *45*, 409.
- (9) Moszynski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1994**, *100*, 1312.
- (10) Moszynski, R.; Cybulski, S. M.; Chalasinski, G. *J. Chem. Phys.* **1994**, *100*, 4998.
- (11) Moszynski, R.; Jeziorski, B.; Rybak, S.; Szalewicz, K.; Williams, H. L. *J. Chem. Phys.* **1994**, *100*, 5080.
- (12) Williams, H. L.; Szalewicz, K.; Moszynski, R.; Jeziorski, B. *J. Chem. Phys.* **1995**, *103*, 4586.
- (13) Bukowski, R.; Cencek, W.; Jankowski, P.; Jeziorska, M.; Jeziorski, B.; Kucharski, S. A.; Lotrich, V. F.; Misquitta, A. J.; Moszynski, R.; Patkowski, K.; Podeszwa, R.; Rybak, S.; Szalewicz, K.; Williams, H. L.; Wheatley, R. J.; Wormer, P. E. S.; Zuchowski, P. S. *SAPT2008: An Ab Initio Program for Many-Body Symmetry-Adapted Perturbation Theory Calculations of Intermolecular Interaction Energies*, University of Delaware and University of Warsaw, 2008; <http://www.physics.udel.edu/~szalewic/SAPT/SAPT.html>.
- (14) Heijmen, T. G. A.; Moszynski, R.; Wormer, P. E. S.; van der Avoird, A. *Mol. Phys.* **1996**, *89*, 81.
- (15) Mas, E. M.; Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **2000**, *113*, 6687.
- (16) Korona, T.; Moszynski, R.; Thibault, F.; Launay, J.-M.; Bussery-Honvault, B.; Boisssoles, J.; Wormer, P. E. S. *J. Chem. Phys.* **2001**, *115*, 3074.
- (17) Bussery-Honvault, B.; Launay, J.-M.; Moszynski, R. *Phys. Rev. A: At. Mol. Opt. Phys.* **2003**, *68*, 032718.
- (18) Jaszunski, M.; McWeeny, R. *Mol. Phys.* **1985**, *55*, 1275.
- (19) Williams, H. L.; Chabalowski, C. F. *J. Phys. Chem. A* **2001**, *105*, 646.
- (20) Jansen, G.; Hesselmann, A. *J. Phys. Chem. A* **2001**, *105*, 11156.
- (21) Misquitta, A. J.; Szalewicz, K. *Chem. Phys. Lett.* **2002**, *357*, 301.

- (22) Misquitta, A. J.; Jeziorski, B.; Szalewicz, K. *Phys. Rev. Lett.* **2003**, *91*, 033201.
- (23) Misquitta, A. J.; Podeszwa, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **2005**, *123*, 214103.
- (24) Hesselmann, A.; Jansen, G. *Chem. Phys. Lett.* **2002**, *357*, 464.
- (25) Hesselmann, A.; Jansen, G. *Chem. Phys. Lett.* **2002**, *362*, 319.
- (26) Hesselmann, A.; Jansen, G. *Chem. Phys. Lett.* **2003**, *367*, 778.
- (27) Hesselmann, A.; Jansen, G. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5010.
- (28) Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. *J. Chem. Phys.* **1979**, *71*, 4993.
- (29) Hesselmann, A.; Jansen, G.; Schütz, M. *J. Chem. Phys.* **2005**, *122*, 014103.
- (30) Hesselmann, A.; Jansen, G.; Schütz, M. *J. Am. Chem. Soc.* **2006**, *128*, 11730.
- (31) Podeszwa, R.; Szalewicz, K. *Chem. Phys. Lett.* **2005**, *412*, 488.
- (32) Podeszwa, R.; Bukowski, R.; Szalewicz, K. *J. Chem. Theory Comput.* **2006**, *2*, 400.
- (33) Podeszwa, R.; Bukowski, R.; Rice, B. M.; Szalewicz, K. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5561.
- (34) Fiethen, A.; Jansen, G.; Hesselmann, A.; Schütz, M. *J. Am. Chem. Soc.* **2008**, *130*, 1802.
- (35) Korona, T.; Hesselmann, A.; Dodziuk, H. *J. Chem. Theor. Comp.* **2009**, *5*, 1585.
- (36) Korona, T.; Jeziorski, B.; Moszynski, R. *Mol. Phys.* **2002**, *100*, 1723.
- (37) Korona, T.; Jeziorski, B. *J. Chem. Phys.* **2006**, *125*, 184109.
- (38) Korona, T. *Phys. Chem. Chem. Phys.* **2007**, *9*, 6004.
- (39) Korona, T.; Jeziorski, B. *J. Chem. Phys.* **2008**, *128*, 144107.
- (40) Korona, T. *J. Chem. Phys.* **2008**, *122*, 224104.
- (41) Korona, T. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5698.
- (42) Korona, T. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6509.
- (43) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 36.
- (44) Bulski, M.; Chalasinski, G.; Jeziorski, B. *Theor. Chim. Acta* **1979**, *52*, 93.
- (45) Chalasinski, G.; Jeziorski, B. *Mol. Phys.* **1976**, *32*, 81.
- (46) Chalasinski, G.; Jeziorski, B. *Theor. Chim. Acta* **1977**, *46*, 477.
- (47) Longuet-Higgins, H. C. *Faraday Discuss. Chem. Soc.* **1965**, *40*, 7.
- (48) Paldus, J.; Jeziorski, B. *Theor. Chim. Acta* **1988**, *73*, 81.
- (49) Moszynski, R.; Żuchowski, P. S.; Jeziorski, B. *Collect. Czech. Chem. Commun.* **2005**, *70*, 1109.
- (50) Jeziorski, B.; Moszynski, R. *Int. J. Quantum Chem.* **1993**, *48*, 161.
- (51) Korona, T.; Przybytek, M.; Jeziorski, B. *Mol. Phys.* **2006**, *104*, 2303.
- (52) Korona, T.; Williams, H. L.; Bukowski, R.; Jeziorski, B.; Szalewicz, K. *J. Chem. Phys.* **1997**, *106*, 5109.
- (53) Williams, H. L.; Mas, E. M.; Szalewicz, K.; Jeziorski, B. *J. Chem. Phys.* **1995**, *103*, 7374.
- (54) Paldus, J. In *Theoretical Chemistry Advances and Perspectives*; Eyring, H., Henderson, D., Eds.; Academic Press: New York, 1976; p 177.
- (55) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *MOLPRO, version 2008.2, a package of ab initio programs*, 2008, see <http://www.molpro.net>.
- (56) Werner, H.-J.; Manby, F. R.; Knowles, P. J. *J. Chem. Phys.* **2003**, *118*, 8149.
- (57) Schütz, M.; Manby, F. R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3349.
- (58) Dunning, Jr., T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer H. F., III, Ed.; Plenum Press: New York, 1977; Vol 2.
- (59) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (60) Kendall, R.; Dunning, T., Jr.; Harrison, R. *J. Chem. Phys.* **1992**, *96*, 6769.
- (61) Weigend, F.; Köhn, A.; Hättig, C. *J. Chem. Phys.* **2002**, *116*, 3175.
- (62) Hättig, C. *Phys. Chem. Chem. Phys.* **2005**, *7*, 59.
- (63) Williams, H. L.; Korona, T.; Bukowski, R.; Szalewicz, K.; Jeziorski, B. *Chem. Phys. Lett.* **1996**, *262*, 431.
- (64) Wada, A.; Kanamori, H.; Iwata, S. *J. Chem. Phys.* **1998**, *109*, 9434.
- (65) Rode, M.; Sadlej, J.; Moszynski, R.; Wormer, P. E. S.; van der Avoird, A. *Chem. Phys. Lett.* **1999**, *314*, 326.
- (66) Milet, A.; Korona, T.; Moszynski, R.; Kochanski, E. *J. Chem. Phys.* **1999**, *111*, 7727.
- (67) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (68) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
- (69) Grüning, M.; Gritsenko, O. V.; van Gisbergen, S. J. A.; Baerends, E. J. *J. Chem. Phys.* **2001**, *114*, 652.
- (70) Computational Chemistry Comparison and Benchmark DataBase, <http://cccbdb.nist.gov>; (accessed July 1, 2008).
- (71) Korona, T.; Moszynski, R.; Jeziorski, B. *J. Chem. Phys.* **1996**, *105*, 8178.
- (72) Ángyán, J. G.; Jansen, G.; Loos, M.; Hättig, C.; Hess, B. A. *Chem. Phys. Lett.* **1994**, *219*, 267.
- (73) Jeziorski, B.; Szalewicz, K. Symmetry-Adapted Perturbation Theory. In *Handbook of Molecular Physics and Quantum Chemistry*; Wilson, S., Ed.; Wiley: New York, 2003; Vol. 3, p 232.
- (74) Kutzelnigg, W.; Mukherjee, D. *J. Chem. Phys.* **1997**, *107*, 432.
- (75) Bukowski, R.; Cencek, W.; Patkowski, K.; Jankowski, P.; Jeziorski, M.; Kolaski, M.; Szalewicz, K. *Mol. Phys.* **2006**, *104*, 2241.