

SAPT: A Program for Many-Body  
Symmetry-Adapted Perturbation Theory  
Calculations of Intermolecular Interaction Energies

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# 1 Introduction

The *ab initio* methods used to calculate the interaction energy can be classified as *supermolecular* and *perturbational*. In a *supermolecular* method the interaction energy is defined as

$$\tilde{E}_{int} = \tilde{E}_{AB} - (\tilde{E}_A + \tilde{E}_B), \quad (1)$$

where  $\tilde{E}_A$ ,  $\tilde{E}_B$ , and  $\tilde{E}_{AB}$  are approximations to the exact ground-state energies  $E_A$ ,  $E_B$ , and  $E_{AB}$  of the monomers A, B, and of the complex AB, respectively. These approximate energies can be computed using any method of solving the clamped-nuclei Schrödinger equation. For typical interactions of closed-shell systems, the exact interaction energy  $E_{int} = E_{AB} - (E_A + E_B)$  is from four to seven orders of magnitude smaller than the total energies  $E_A$ ,  $E_B$ , and  $E_{AB}$ . Since, even with the present supercomputer capabilities, the errors  $E_{AB} - \tilde{E}_{AB}$ ,  $E_A - \tilde{E}_A$ , and  $E_B - \tilde{E}_B$  are always much larger than the interaction energy itself,  $\tilde{E}_{int}$  can be a good approximation to  $E_{int}$  only if a fortunate cancellation of these large errors occurs. For certain approximate methods such a cancellation apparently takes place, although this fact has never been proven *a priori* in a convincing way. There are some necessary (although not sufficient) conditions which a supermolecular approach has to fulfill to provide a reasonable description of the intermolecular interaction: (i) the method has to be extensive and size-consistent [1], (ii) it has to sufficiently well account for the electron correlation, and (iii) the approximate monomer energies  $\tilde{E}_A$  and  $\tilde{E}_B$  have to be calculated using the full orbital basis of the complex AB [2, 3, 4, 5, 6, 7, 8, 9, 10].

*Perturbational* methods [11, 12] compute the interaction energy  $E_{int}$  directly (i.e. no subtraction of much larger quantities is involved), as a sum of physically distinct contributions

$$E_{int} = E_{pol}^{(1)} + E_{exch}^{(1)} + E_{pol}^{(2)} + E_{exch}^{(2)} + \dots, \quad (2)$$

where  $E_{pol}^{(1)}$  is the damped classical electrostatic interaction energy,  $E_{pol}^{(2)}$  is a sum of the damped classical induction and quantum mechanical dispersion energies

$$E_{pol}^{(2)} = E_{ind}^{(2)} + E_{disp}^{(2)} \quad (3)$$

and  $E_{exch}^{(n)}$ ,  $n=1,2$  are exchange corrections defined by the symmetry-adapted perturbation theory (SAPT) [11, 12, 13]. The exchange corrections can be physically interpreted as an effect of the resonance tunneling of electrons between the interacting systems. In the perturbational methods the clamped nuclei Hamiltonian  $H$  for the complex AB is divided into the unperturbed operator  $H_0$  being the sum of the Hamiltonians for molecules A and B, i.e.  $H_0 = H_A + H_B$ , and the interaction operator  $V$  defined as the difference  $V = H - H_0$ . The polarization corrections  $E_{pol}^{(n)}$  are the coefficients in the Taylor expansion of the ground-state eigenvalue  $E(\zeta)$  of the Hamiltonian  $H(\zeta) = H_0 + \zeta V$ , i.e., these corrections are identical with the Rayleigh-Schrödinger (RS) perturbation energies corresponding to the partitioning  $H = H_0 + V$ . Since the RS method completely neglects the exchange of electrons, it is called, after Hirschfelder [14], the *polarization expansion*. In this theory  $V$  is *not* expressed in terms of the multipole expansion [15], therefore the damping effect of the penetration (the charge overlap) is properly taken into account. Thus, the polarization energies  $E_{pol}^{(n)}$  have a well defined meaning for all intermolecular distances.

It should be noted that the exchange corrections  $E_{exch}^{(n)}$  obtained in SAPT are not unique for  $n > 1$ . Different formulations of SAPT [12, 16, 17, 18, 19, 20] lead to different expressions for  $E_{exch}^{(n)}$  and, consequently, to different convergence rates of the expansion (2) [21, 22, 23]. For the van der Waals interactions of nonpolar and weakly polarizable systems the differences between various SAPT expansions are not important because the interaction energy is dominated by the first three terms in the expansion (2) and, moreover, the second-order exchange energies  $E_{exch}^{(n)}$  in various SAPT schemes do not differ significantly. Among different formulations of the symmetry-adapted perturbation theories (see, e.g., Refs. [12, 13] for a review), the Symmetrized Rayleigh-Schrödinger (SRS) perturbation theory [22, 23, 24] has

been found to be the most suitable to study weak intermolecular interactions. The perturbation equations of the SRS theory can be efficiently solved for many-electron systems. When applied through the second-order to systems for which the interaction energy is known to a high precision – such as  $2p\sigma_u$  state of  $H_2^+$  [22],  $b\ ^3\Sigma_u$  state of  $H_2$  [25],  $X\ ^1\Sigma_g$  state of  $He_2$  [26, 27, 28], Ar- $H_2$  [30], and Ar-HF [84] – this method has been shown to reproduce the interaction energies very accurately. The method has been also applied to systems for which the interaction potentials were not known very well – such as He- $F^-$  [29], water dimer, HF dimer, and uracil-water – and produced the interaction energies which we believe are more accurate than available literature results.

Since neither the exact eigenfunctions of  $H_0$ , nor even some reasonable approximations to them, can be computed in practice for any but two-electron molecules, one has to use the HF-SCF determinants as the starting point and apply some kind of multiple perturbation theory to take account of the intramonomer electron correlation. The monomer Hamiltonians  $H_A$  and  $H_B$  are decomposed as  $H_A = F_A + W_A$  and  $H_B = F_B + W_B$ , where  $F_A$  and  $F_B$  are the Fock operators for molecules A and B, respectively (the Møller-Plesset partitioning). Thus, the total Hamiltonian can be written as

$$H(\zeta, \lambda_A, \lambda_B) = F + \zeta V + \lambda_A W_A + \lambda_B W_B, \quad (4)$$

where  $F = F_A + F_B$  and the formal expansion parameters  $\zeta$ ,  $\lambda_A$ , and  $\lambda_B$  have the physical value equal to unity. By applying the triple RS-type perturbation theory one can derive a many-body expansion of the corrections  $E_{pol}^{(n)}$  in terms of the correlation operators (or fluctuation potentials)  $W_A$  and  $W_B$  of individual monomers

$$E_{pol}^{(n)} = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} E_{pol}^{(nij)}, \quad (5)$$

where  $E_{pol}^{(nij)}$  is of the  $n$ th order in  $V$ , of the  $i$ th order in  $W_A$ , and of the  $j$ th order in  $W_B$ . The corrections  $E_{pol}^{(nij)}$  are formally defined as the coefficients in the Taylor expansion of the ground-state eigenvalue  $E(\zeta, \lambda_A, \lambda_B)$  of  $H(\zeta, \lambda_A, \lambda_B)$ . The expansion (5) and a similar expansion for the exchange components  $E_{exch}^{(n)}$  have been

introduced in Refs. [26] and [13] and the general method of expanding individual terms in Eq. (5) through one- and two-electron integrals (perturbation theory diagrams) has been developed in Refs. [31, 32, 33, 34]. When the expansion (5) (and a similar expansion for  $E_{exch}^{(n)}$ ) is inserted into Eq. (2), one obtains a many-body SAPT expansion for the total interaction energy. The corrections  $E_{pol}^{(n00)}$  and  $E_{exch}^{(n00)}$  can be viewed as describing the interaction of “Hartree-Fock” molecules, while the remaining terms in the expansion (5), i.e.  $E_{pol}^{(n)} - E_{pol}^{(n00)}$  and  $E_{exch}^{(n)} - E_{exch}^{(n00)}$ , represent the intramonomer correlation effect.

The intramonomer correlation corrections are obviously more difficult to evaluate than the leading term  $E^{(n00)}$  in Eq. (5). A derivation of a many-body expansion for the exchange energies is even more difficult because of the necessity to handle overlap integrals for nonorthogonal sets of orbitals. When the intramonomer correlation is neglected, this nonorthogonality is manageable and the problem was solved some time ago both in the case of the first-order exchange energy [35]  $E_{exch}^{(100)}$  and the exchange-induction  $E_{exch-ind}^{(200)}$  and exchange-dispersion  $E_{exch-disp}^{(200)}$  energies [36]. Among all the intramonomer correlation contributions to the exchange energies only the corrections of the first order in  $V$  can be expected to give a nonnegligible contribution.

In Sec. 2 we present a general formulation of the polarization expansion for the interaction energy based on the Coupled-Cluster (CC) form of the Schrödinger equation [37, 38, 39]. This formulation leads to the many-body theory in which only connected quantities appear and one does not have to perform explicitly cancellations of unlinked diagrams [40]. The leading intramonomer correlation contributions to the electrostatic energy are considered in Sec. 3, while Sec. 4 contains discussion of the many-body expansion of the first-order exchange energy. Sections 5 and 6 give the formulas for the leading-order induction and exchange-induction corrections, respectively. In Sec. 7 we present the many-body expansion of the dispersion energy, while Sec. 8 gives the formula for the leading order exchange-dispersion energy. To help understanding the meaning of various contributions to the interaction energy we present in Table 1 the list of all perturbation theory corrections considered in

this work together with their physical interpretation and a reference to the equations defining them. Finally, Sec. 9 contains a general discussion and conclusions.

## 2 Many-body expansion of the interaction energy

The standard, generally accepted definitions of the dispersion energy  $E_{disp}^{(2)}$  and other SAPT corrections involve *nonsymmetric* operators like  $H_0 = H_A + H_B$  or  $V$ . These operators do not include all electrons in a fully symmetric way and, consequently, do not preserve the antisymmetry property of the wave functions upon which they act. Thus,  $H_0$  and  $V$  are not legitimate operators in the conventional antisymmetric Hilbert space  $\mathcal{H}$  for  $N = N_A + N_B$  electrons ( $N_C$ ,  $C = A$  or  $B$ , is the number of electrons of the molecule C). To use these operators we have to consider a larger space  $\mathcal{H}_A \otimes \mathcal{H}_B$  being the tensor product of Hilbert spaces  $\mathcal{H}_A$  and  $\mathcal{H}_B$  for molecules A and B. The Hilbert spaces  $\mathcal{H}_A$  and  $\mathcal{H}_B$  are individually antisymmetric, i.e. they contain only antisymmetric functions of  $N_A$  and  $N_B$  electrons, respectively. Thus,  $\mathcal{H}_A \otimes \mathcal{H}_B$  includes all functions of  $N_A + N_B$  electronic coordinates which are antisymmetric with respect to permutations of electrons *within* each of the monomers. Permutations of electrons between interacting molecules may generally change the wave functions from  $\mathcal{H}_A \otimes \mathcal{H}_B$  in a nontrivial fashion. Since  $\mathcal{H} \subset \mathcal{H}_A \otimes \mathcal{H}_B$ , all physical solutions of the Schrödinger equation belong to  $\mathcal{H}_A \otimes \mathcal{H}_B$ . It should be pointed out that the dispersion energy  $E_{disp}^{(2)}$  cannot be defined using the fully antisymmetric Hilbert space  $\mathcal{H}$  and the introduction of  $\mathcal{H}_A \otimes \mathcal{H}_B$  is necessary.

### 2.1 Second-quantization formalism for nonsymmetric operators

To introduce an appropriate second-quantization formalism for nonsymmetric operators we have to consider the generalized Fock space  $\mathcal{F}_{AB} = \mathcal{F}_A \otimes \mathcal{F}_B$ , where  $\mathcal{F}_C$ ,  $C=A$  or  $B$ , is the usual Fock space for the electrons of the molecule C. The

annihilation (creation) operators acting in  $\mathcal{F}_A$  and  $\mathcal{F}_B$  will be denoted by  $a_\mu$  ( $a_\mu^\dagger$ ) and  $b_\mu$  ( $b_\mu^\dagger$ ), respectively. These operators satisfy the following (anti)commutation relations

$$\{a_\mu, a_\nu\} = \{b_\mu, b_\nu\} = \{a_\mu^\dagger, a_\nu^\dagger\} = \{b_\mu^\dagger, b_\nu^\dagger\} = 0, \quad (6)$$

$$\{a_\mu^\dagger, a_\nu\} = \{b_\mu^\dagger, b_\nu\} = \delta_{\mu\nu}, \quad (7)$$

$$[a_\mu, b_\nu] = [a_\mu^\dagger, b_\nu] = [a_\mu, b_\nu^\dagger] = [a_\mu^\dagger, b_\nu^\dagger] = 0, \quad (8)$$

where  $[ , ]$  and  $\{ , \}$  denote the commutator and anticommutator, respectively. Eqs. (6) and (7) are a consequence of the orthonormality of the spinorbital basis set  $\phi_\mu^A(\phi_\mu^B)$  used to define  $a_\mu(b_\mu)$ . Eq. (8) results from the fact that the operators  $a_\mu$  and  $b_\mu$  act on different sets of variables. This means that the electrons of the molecules A and B are treated as different, *distinguishable* particles. This is not an approximation since any antisymmetric function  $\Psi$  can be expanded in terms of the product functions  $\Psi_A \Psi_B \in \mathcal{H}_A \otimes \mathcal{H}_B$  so that the Schrödinger equation  $H\Psi = E\Psi$  can still be exactly fulfilled in  $\mathcal{F}_{AB}$ . However, one should be aware of the fact that  $\mathcal{F}_{AB}$  contains also solutions of the Schrödinger equations which do not correspond to any physical states of the complex AB since they violate the Pauli principle.

Using the creation and annihilation operators one can write the operators  $F_C$  and  $W_C$ ,  $C=A$  or  $B$ , in the following second-quantized form

$$F_C = (f_C)_\nu^\mu c_\mu^\nu, \quad (9)$$

$$W_C = \frac{1}{4} w_{\mu\nu}^{\lambda\kappa} c_{\lambda\kappa}^{\mu\nu} - w_{\nu\gamma}^{\mu\gamma} c_\mu^\nu, \quad \gamma \in C, \quad (10)$$

where  $(f_C)_\nu^\mu$  are the matrix elements of the Fock operator for molecule C,  $w_{\mu\nu}^{\lambda\kappa}$  are the antisymmetrized two electron integrals

$$w_{\mu\nu}^{\lambda\kappa} = \langle \phi_\mu(1)\phi_\nu(2) | r_{12}^{-1}(1 - P_{12})\phi_\lambda(1)\phi_\kappa(2) \rangle \quad (11)$$

and the symbol  $c_{\mu\nu\dots}^{\lambda\kappa\dots}$ ,  $c = a$  or  $b$ , denotes the operator product

$$c_{\mu\nu\dots}^{\lambda\kappa\dots} = c_\lambda^\dagger c_\kappa^\dagger \dots c_\nu c_\mu. \quad (12)$$

Summation over repeated *lower and upper* indices is implied in Eqs. (9), (10) and throughout the rest of this paper (the Einstein convention). We shall also always assume that  $\alpha, \beta, \gamma, \delta$  ( $\rho, \sigma, \tau, \omega$ ) label occupied (virtual) spinorbitals while  $\lambda, \kappa, \mu, \nu$  are used when all spinorbitals (both occupied and unoccupied) can occur in a summation or in a formula. It will be clear from the context whether the indices  $\lambda, \kappa, \mu, \nu$  pertain to spinorbitals of molecule A or molecule B. However, we shall always assume that lower case Greek letters  $\alpha$  and  $\rho$  ( $\beta$  and  $\sigma$ ) label the spinorbitals of molecule A (molecule B). The intermolecular interaction operator  $V$  can be represented in the form

$$V = v_{\mu\nu}^{\lambda\kappa} a_{\lambda}^{\mu} b_{\kappa}^{\nu} + (v_A)_{\mu}^{\lambda} b_{\lambda}^{\mu} + (v_B)_{\nu}^{\kappa} a_{\kappa}^{\nu} + V_0, \quad (13)$$

where  $V_0$  is the constant nuclear repulsion term,

$$v_{\mu\nu}^{\lambda\kappa} = \langle \phi_{\mu}(1) \phi_{\nu}(2) | r_{12}^{-1} | \phi_{\lambda}(1) \phi_{\kappa}(2) \rangle, \quad (14)$$

and  $(v_C)_{\mu}^{\nu} = \langle \phi_{\mu} | v_C | \phi_{\nu} \rangle$  is a matrix element of the electrostatic potential

$$v_C(\mathbf{r}_i) = - \sum_{\alpha \in C} \frac{Z_{\alpha}}{r_{\alpha i}}, \quad (15)$$

of all the nuclei of molecule C.  $Z_{\alpha}$  denotes here the charge of the  $\alpha$ th nucleus and  $r_{\alpha i}$  the distance of electron  $i$  from this nucleus.

Equations (9) and (10) are the standard expressions of the second-quantization theory [39]. To prove Eq. (13) it is enough to verify that the matrix elements of  $V$  in the basis of products of Slater determinants are the same as the matrix elements of the first-quantized operator

$$V = \sum_{i \in A}^{N_A} v_B(\mathbf{r}_i) + \sum_{j \in B}^{N_B} v_A(\mathbf{r}_j) + \sum_{i \in A}^{N_A} \sum_{j \in B}^{N_B} r_{ij}^{-1} + V_0. \quad (16)$$

One can easily check that the operators  $F_C$ ,  $W_C$ ,  $V$ , and  $H$  commute with the number operators  $\hat{N}_A = a_{\mu}^{\mu}$  and  $\hat{N}_B = b_{\mu}^{\mu}$  and, consequently, conserve the number of electrons in molecule A (or B). This means that we can limit ourselves to the  $(N_A + N_B)$ -electron Hilbert space  $\mathcal{H}_A \otimes \mathcal{H}_B$  and need not consider the Fock space  $\mathcal{F}_{AB}$  any further.



One should mention that the spinorbitals  $\phi_\mu^C$  do not have to be localized on the nuclei of molecule C (monomer-centered basis). All further development remains valid also when  $\phi_\mu^C$ 's are localized on the nuclei of both molecules (dimer-centered basis). In particular the linear spans of  $\phi_\mu^A$ 's and  $\phi_\mu^B$ 's can be identical. The use of the dimer-centered basis set is essential for calculating the exchange components of the interaction energy.

As is well known, formulae (9)-(14) are invariant under unitary transformations of spinorbitals  $\phi_\mu^C$ . For perturbation theory development, however, it is very convenient to use the *canonical* spinorbitals which diagonalize the Fock operator  $f_C$

$$(f_C)_\nu^\mu = \langle \phi_\mu^C | f_C | \phi_\nu^C \rangle = \epsilon_\mu^C \delta_{\mu\nu}, \quad (17)$$

where  $\epsilon_\mu^C$  are the orbital energies. These orbitals will be used in all further considerations.

## 2.2 Explicitly connected polarization expansion

The Schrödinger equation for the complex AB

$$(F + \zeta V + \lambda_A W_A + \lambda_B W_B)\Psi = E\Psi \quad (18)$$

can be solved using the conventional Rayleigh-Schrödinger perturbation theory in which  $F = F_A + F_B$  is treated as the unperturbed operator and  $V$ ,  $W_A$ , and  $W_B$  are perturbations. The corresponding zeroth-order equation is

$$F\Phi = E_0\Phi. \quad (19)$$

It is easy to see that the unperturbed wave function  $\Phi = \Phi_A\Phi_B$  is the product of the HF determinants  $\Phi_A$  and  $\Phi_B$  for monomers A and B, and  $E_0$  is the sum of the orbital energies of all occupied orbitals in A and B. In the conventional approach the perturbation corrections  $E_{pol}^{(kij)}$  are expressed in terms of  $\Phi$ ,  $V$ ,  $W_A$ ,  $W_B$  and the reduced resolvent of  $F$ . The expressions for  $E_{pol}^{(kij)}$  contain many components, which, after expansion in terms of one- and two-electron integrals, contain disconnected

terms (or diagrams) and, consequently, behave incorrectly when the size of the system increases. After considerable algebraic manipulations these disconnected terms cancel out in each order of perturbation theory and the final result contains only connected terms (or diagrams), which guarantees the extensivity [1] of the energy. To avoid the above complications we found it advantageous to formulate the perturbation theory using the coupled-cluster representation of the Schrödinger equation [37, 38, 39, 40]. In this representation the nonphysical disconnected terms do not appear at all and the perturbation energies are expressed directly in terms of connected contributions.

The coupled-cluster ansatz for the exact wave function  $\Psi$  is [27]

$$\Psi = e^T \Phi, \quad (20)$$

where

$$T = \sum_{n=0}^{N_A} \sum_{m=0}^{N_B} T_{nm}, \quad n + m > 0 \quad (21)$$

is the cluster operator which creates  $n$ -tuple excitations of the monomer A and  $m$ -tuple excitations of the monomer B. The explicit form of the operator  $T_{nm}$  is

$$T_{nm} = \left(\frac{1}{n!m!}\right)^2 t_{\rho_1 \dots \rho_n \sigma_1 \dots \sigma_m}^{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m} a_{\alpha_1 \dots \alpha_n}^{\rho_1 \dots \rho_n} b_{\beta_1 \dots \beta_m}^{\sigma_1 \dots \sigma_m}, \quad (22)$$

where the indices  $\alpha_1 \dots \alpha_n$  and  $\rho_1 \dots \rho_n$  label spinorbitals of the monomer A and the indices  $\beta_1 \dots \beta_m$  and  $\sigma_1 \dots \sigma_m$  label spinorbitals of the monomer B. We assume that the cluster amplitudes  $t$  are separately antisymmetric in the four groups of their indices  $\alpha_1 \dots \alpha_n$ ,  $\beta_1 \dots \beta_m$ ,  $\rho_1 \dots \rho_n$ , and  $\sigma_1 \dots \sigma_m$ . The  $t$ -amplitudes and the  $T_{nm}$  operators are then uniquely defined by  $\Psi$ . The ansatz (20) differs from the standard fully antisymmetric exponential ansatz of the coupled-cluster theory [37, 38, 41, 1] since  $\Phi = \Phi_A \Phi_B$  is the product of two Slater determinants rather than a single determinant.

The cluster operator  $T$  and the total energy are determined from the Schrödinger equation  $(H - E)\Psi = 0$ . Writing this equation in the form  $e^{-T}(H - E)e^T \Phi = 0$  and projecting against the functions

$$\Phi_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m}^{\rho_1 \dots \rho_n \sigma_1 \dots \sigma_m} = a_{\alpha_1 \dots \alpha_n}^{\rho_1 \dots \rho_n} b_{\beta_1 \dots \beta_m}^{\sigma_1 \dots \sigma_m} \Phi.$$

gives the following equation for  $T$ :

$$\langle \Phi_{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m}^{\rho_1 \dots \rho_n \sigma_1 \dots \sigma_m} | e^{-T} (F + \zeta V + \lambda_A W_A + \lambda_B W_B) e^T \Phi \rangle = 0. \quad (23)$$

Note, that the cluster operator  $T$  depends now on the expansion parameters  $\zeta$ ,  $\lambda_A$  and  $\lambda_B$ , i.e.  $T = T(\zeta, \lambda_A, \lambda_B)$ . Similarly, projecting against  $\Phi$  we obtain the energy expression

$$E(\zeta, \lambda_A, \lambda_B) = E_0 + \langle (\zeta V + \lambda_A W_A + \lambda_B W_B) e^T \rangle, \quad (24)$$

where  $\langle X \rangle$  is the “vacuum” expectation value of the operator  $X$

$$\langle X \rangle = \langle \Phi | X \Phi \rangle.$$

No approximations have been made in deriving Eqs. (23) and (24) so that for  $\zeta = \lambda_A = \lambda_B = 1$  all the exchange effects are included in  $E(1, 1, 1)$ . The exchange is neglected when a *finite-order* power series in  $\zeta$  is used to approximate  $E(\zeta, \lambda_A, \lambda_B)$  at  $\zeta = 1$  (Refs. [21, 22, 23]). The polarization corrections  $E_{pol}^{(n)}$  are then defined as the coefficients in the power series expansion of  $E(\zeta, 1, 1)$ . Similarly, the intramonomer correlation corrections  $E_{pol}^{(nij)}$  are coefficients in the triple power series expansion of  $E(\zeta, \lambda_A, \lambda_B)$  around  $\zeta = \lambda_A = \lambda_B = 0$ .

It is easy to verify that when  $\zeta = 0$

$$T(0, \lambda_A, \lambda_B) = T_A(\lambda_A) + T_B(\lambda_B) \quad (25)$$

and

$$E(0, \lambda_A, \lambda_B) = E_A(\lambda_A) + E_B(\lambda_B), \quad (26)$$

where  $T_A(\lambda_A)$  and  $T_B(\lambda_B)$  are the exact cluster operators for the molecule A and B, respectively, and  $E_A(\lambda_A)$  and  $E_B(\lambda_B)$  are the ground-state eigenvalues of the Hamiltonians  $F_A + \lambda_A W_A$  and  $F_B + \lambda_B W_B$ . It follows from Eqs. (25) and (26) that  $T^{(0ij)}$  and  $E_{pol}^{(0ij)}$  must vanish when  $i > 0$  and  $j > 0$ . The corrections  $E_{pol}^{(0i0)}$  and  $E_{pol}^{(00j)}$  are just the Møller-Plesset perturbation energies for molecules A and B, respectively. All the remaining corrections  $E_{pol}^{(nij)}$ ,  $n \geq 1$ , must therefore be included in the interaction energy  $E_{int}$ . Since  $T_A(\lambda_A)$  and  $T_B(\lambda_B)$  are the sums of

the operators of the form  $T_{n0}$  and  $T_{0n}$ , respectively, Eq. (25) shows that all cluster operators  $T_{nm}$  for which  $n > 0$  and  $m > 0$  must vanish when  $\zeta \rightarrow 0$ , i.e., when the interaction between monomers is switched off.

In the following we shall also use double-superscript energy corrections  $E_{pol}^{(kl)}$  and  $E_{exch}^{(kl)}$  defined generally by

$$E^{(kl)} = \sum_{i=0}^l E^{(k,i,l-i)}.$$

They represent the intramonomer correlation effect of the  $l$ th order in the total correlation operator  $W = W_A + W_B$ .

To proceed further, Eq. (23) has to be transformed into a form suitable for an iterative (perturbative) solution. Using the fact that

$$e^{-T} F e^T = F + [F, T]$$

it can be rewritten in the form

$$\langle a_{\alpha_1 \dots \alpha_n}^{\rho_1 \dots \rho_n} b_{\beta_1 \dots \beta_m}^{\sigma_1 \dots \sigma_m} \Phi \mid [F, T] + D \mid \Phi \rangle = 0, \quad (27)$$

where  $D = e^{-T}(\zeta V + \lambda_A W_A + \lambda_B W_B) e^T$ . After the commutator in Eq. (27) is expanded using, e.g., the contraction theorem [42], one obtains

$$-\epsilon_{\rho_1 \dots \rho_n \sigma_1 \dots \sigma_m}^{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m} t_{\rho_1 \dots \rho_n \sigma_1 \dots \sigma_m}^{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m} + \langle a_{\alpha_1 \dots \alpha_n}^{\rho_1 \dots \rho_n} b_{\beta_1 \dots \beta_m}^{\sigma_1 \dots \sigma_m} \Phi \mid D \mid \Phi \rangle = 0, \quad (28)$$

where

$$\epsilon_{\rho_1 \dots \rho_n \sigma_1 \dots \sigma_m}^{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m} = \epsilon_{\alpha_1}^A + \dots + \epsilon_{\alpha_n}^A + \epsilon_{\beta_1}^B + \dots + \epsilon_{\beta_m}^B - \epsilon_{\rho_1}^A - \dots - \epsilon_{\rho_n}^A - \epsilon_{\sigma_1}^B - \dots - \epsilon_{\sigma_m}^B.$$

Note that there is no implicit summation in the formula (28) since the repeated indices are either both lower or both upper. For fixed  $D$  Eq. (28) can be easily solved for  $T_{nm}$ . This solution can be written formally as  $T_{nm} = \mathfrak{R}_{nm}(D)$ , where  $\mathfrak{R}_{nm}$  is the resolvent superoperator defined for an arbitrary operator  $X$  as [27]

$$\mathfrak{R}_{nm}(X) = \left(\frac{1}{n!m!}\right)^2 \langle a_{\rho_1 \dots \rho_n}^{\alpha_1 \dots \alpha_n} b_{\sigma_1 \dots \sigma_m}^{\beta_1 \dots \beta_m} X \rangle a_{\alpha_1 \dots \alpha_n}^{\rho_1 \dots \rho_n} b_{\beta_1 \dots \beta_m}^{\sigma_1 \dots \sigma_m} / \epsilon_{\rho_1 \dots \rho_n \sigma_1 \dots \sigma_m}^{\alpha_1 \dots \alpha_n \beta_1 \dots \beta_m}. \quad (29)$$

The definition (29) represents a natural generalization of the resolvent superoperator introduced in Ref. [43]. Equation (21) allows us now to rewrite Eq. (23) in the form

$$T = \Re(e^{-T}(\zeta V + \lambda_A W_A + \lambda_B W_B)e^T), \quad (30)$$

where

$$\Re = \sum_{n=0}^{N_A} \sum_{m=0}^{N_B} \Re_{nm}, \quad n + m > 0. \quad (31)$$

Equation (30) is ideally suited for perturbative or iterative solution. If an iterative procedure is initiated by assuming  $T = 0$  (note that for  $\zeta = \lambda_A = \lambda_B = 0$  we have  $T = 0$ ), it generates polynomials in  $\zeta, \lambda_A, \lambda_B$  which after sufficiently many iterations provide the expressions for the coefficients in the series

$$T(\zeta, \lambda_A, \lambda_B) = \sum_{kij} \zeta^k \lambda_A^i \lambda_B^j T^{(kij)}, \quad k + i + j > 0. \quad (32)$$

Alternatively, substituting Eq. (32) into Eq. (30) and comparing coefficients at  $\zeta^k \lambda_A^i \lambda_B^j$  gives recursive relations for  $T^{(kij)}$ . Inserting Eq. (32) into Eq. (24) one obtains the formulas for the individual corrections  $E_{pol}^{(kij)}$ . In transforming Eq. (30) the following (finite) expansion is used

$$e^{-T} X e^T = X + [X, T] + \frac{1}{2!} [[X, T], T] + \dots \quad (33)$$

which shows that all the  $T^{(kij)}$  operators and all the energy corrections  $E_{pol}^{(kij)}$  are expressed through commutators. Since a commutator of two second-quantized operators contains only contracted (connected) terms (diagrams), our perturbation energies and cluster operators are fully connected. Disconnected (size nonextensive) objects do not appear in the theory at all and do not have to be eliminated. This feature of our approach not only simplifies an order-by-order perturbation theory expansion but also allows a nonperturbative treatment of intramonomer correlation effects via size-extensive infinite-order (in  $W_A$  or  $W_B$ ) selective summation techniques.

## 2.3 Explicitly connected expansion of exchange corrections

The simplest way to obtain the exchange contribution in a low-order perturbation treatment is to keep Eq. (23) intact and to introduce antisymmetrization into the energy expression. The appropriate energy expression is [22, 23]

$$\mathcal{E}_{int}(\zeta, \lambda_A, \lambda_B) = \langle \Psi_A \Psi_B | \zeta V \mathcal{A} e^T \Phi \rangle / \langle \Psi_A \Psi_B | \mathcal{A} e^T \Phi \rangle, \quad (34)$$

where  $\Psi_X$  is the exact *normalized* wave function of the monomer  $X$ ,  $T = T(\zeta, \lambda_A, \lambda_B)$  is defined by Eq. (23), and  $\mathcal{A}$  is the full  $N$ -electron antisymmetrizer. Equation (34) is obtained when the Schrödinger equation  $(H - E)e^T \Phi = 0$  is replaced by the antisymmetrized form  $(H - E)\mathcal{A}e^T \Phi = 0$  and the scalar product of the l.h.s. with  $\Psi_A \Psi_B$  is set equal to zero. This method of introducing the exchange terms is equivalent to the so-called symmetrized-polarization method of Chipman *et al.* [18] or the Symmetrized Rayleigh-Schrödinger (SRS) method of Ref. [22]. The latter method is identical [25] to the generalized Heitler-London method recently proposed by Tang and Toennies [44]. Other, more complicated methods of symmetry adaptation are possible [22, 23] but through the second order in  $V$  they lead to results equivalent to those of the SRS method. It should be stressed that  $\mathcal{E}(\zeta, \lambda_A, \lambda_B)$  and  $E(\zeta, \lambda_A, \lambda_B)$  are two different analytic functions of  $\zeta$ ,  $\lambda_A$ , and  $\lambda_B$ , though they are equal for  $\zeta = \lambda_A = \lambda_B = 1$ , i.e.

$$\mathcal{E}(1, 1, 1) = E(1, 1, 1). \quad (35)$$

The exchange corrections to the interaction energy are defined by

$$E_{exch}^{(nij)} = E^{(nij)} - E_{pol}^{(nij)}, \quad (36)$$

where  $E^{(nij)}$  are the coefficients in the Taylor expansion of  $\mathcal{E}(\zeta, \lambda_A, \lambda_B)$

$$\mathcal{E}(\zeta, \lambda_A, \lambda_B) = \sum_{nij} \zeta^n \lambda_A^i \lambda_B^j E^{(nij)}. \quad (37)$$

To derive practically applicable expressions for the exchange corrections we have to introduce the single-exchange approximation. To this end the antisymmetrizer  $\mathcal{A}$  is written as

$$\mathcal{A} = \frac{N_A! N_B!}{(N_A + N_B)!} \mathcal{A}_A \mathcal{A}_B (1 + P_1 + P'), \quad (38)$$

where  $\mathcal{A}_X$ ,  $X=A$  or  $B$ , is the antisymmetrizer of the monomer  $X$ , and  $P_1$  and  $P'$  collect intermolecular exchanges of one and more pairs of electrons, respectively. The single-exchange operator  $P_1$  is given explicitly by

$$P_1 = - \sum_{i \in A} \sum_{j \in B} P_{ij}, \quad (39)$$

where  $P_{ij}$  is the operator interchanging the coordinates of the  $i$ th and  $j$ th electron. The operator  $P'$  can be similarly written as the sum of operators interchanging simultaneously the coordinates of more than two electrons.

The first-order interaction energy in the SRS perturbation theory is given by

$$E^{(1)} = \frac{\langle \Psi_A \Psi_B | V \mathcal{A} \Psi_A \Psi_B \rangle}{\langle \Psi_A \Psi_B | \mathcal{A} \Psi_A \Psi_B \rangle}. \quad (40)$$

and is usually represented as the sum of the electrostatic and exchange contributions

$$E^{(1)} = E_{pol}^{(1)} + E_{exch}^{(1)}, \quad (41)$$

where the electrostatic part  $E_{pol}^{(1)}$  is defined by

$$E_{pol}^{(1)} = \langle \Psi_A \Psi_B | V \Psi_A \Psi_B \rangle. \quad (42)$$

Neglecting terms of the fourth and higher-order in the intermolecular overlap densities  $\rho_{\kappa\mu}(\mathbf{r}) = \phi_{\kappa}^A(\mathbf{r})\phi_{\mu}^B(\mathbf{r})$ , the main, single-exchange part of  $E_{exch}^{(1)}$  is given by [45, 46]

$$E_{exch}^{(1)}(S^2) = \langle \Psi_A \Psi_B | V P_1 \Psi_A \Psi_B \rangle - E_{pol}^{(1)} \langle \Psi_A \Psi_B | P_1 \Psi_A \Psi_B \rangle. \quad (43)$$

The role of the term proportional to  $E_{pol}^{(1)}$  in this equation is to cancel the unlinked clusters appearing when the expression  $\langle \Psi_A \Psi_B | V P_1 \Psi_A \Psi_B \rangle$  is expanded in terms of eigenfunctions of the Fock operators  $f_A$  and  $f_B$  of the monomers  $A$  and  $B$ , respectively.

The second-order exchange energy in the single-exchange approximation is given by

$$E_{exch}^{(2)} = \langle \Psi_A \Psi_B | (V - E_{pol}^{(1)})(P_1 - \bar{P}_1) \Psi^{(1)} \rangle, \quad (44)$$

where  $\bar{P}_1 = \langle \Psi_A \Psi_B | P_1 \Psi_A \Psi_B \rangle$ , and  $\Psi^{(1)}$  is the first-order wave function in the polarization approximation. It can be shown [36] that the first-order wave function

$\Psi^{(1)}$  naturally decomposes into the induction and dispersion parts

$$\Psi^{(1)} = \Psi_{ind}^{(1)} + \Psi_{disp}^{(1)}, \quad (45)$$

so that the second-order exchange energy can be represented as a sum of two distinct exchange terms representing the coupling of the electron exchange with the induction and dispersion interactions

$$E_{exch}^{(2)} = E_{exch-ind}^{(2)} + E_{exch-disp}^{(2)}. \quad (46)$$

The explicit expression for the exchange-induction ( $E_{exch-ind}^{(2)}$ ) and exchange-dispersion ( $E_{exch-disp}^{(2)}$ ) energies are given by

$$E_{exch-ind}^{(2)} = \langle \Psi_A \Psi_B | (V - E_{pol}^{(1)})(P_1 - \bar{P}_1) \Psi_{ind}^{(1)} \rangle, \quad (47)$$

$$E_{exch-disp}^{(2)} = \langle \Psi_A \Psi_B | (V - E_{pol}^{(1)})(P_1 - \bar{P}_1) \Psi_{disp}^{(1)} \rangle. \quad (48)$$

Similarly as in the case of the first-order exchange energy, the second-order exchange energy could be represented as a commutator expansion showing its connected and size-extensive character. Since for model systems [22, 25] the second-order exchange energy is one-order of magnitude smaller than the first-order contribution, we will approximate the exchange-induction and exchange-dispersion energies by the leading-order corrections of their many-body expansions, i.e., by  $E_{exch-ind}^{(200)}$  and  $E_{exch-disp}^{(200)}$ , respectively.

### 3 Electrostatic energy

The electrostatic energy  $E_{pol}^{(1)}$  plays a major role in determining both the structure and energetics of van der Waals complexes [48]. At large intermolecular distances  $E_{pol}^{(1)}$  can be represented as a classical electrostatic interaction between the permanent multipole moments of unperturbed monomers. However, one cannot regard the electrostatic energy as a purely classical effect, because of the quantum-mechanical origin of the charge distributions in molecules and because of the charge overlap or penetration effects. Contemporary understanding of intermolecular electrostatics



evolved from the theories developed by Buckingham [48]. Unfortunately, purely multipolar description of the electrostatic effects encounters serious problems because of the divergent nature of the multipole expansion. Several approximate models have been proposed to describe the electrostatic interactions [49, 50, 51, 52] of small and medium size molecules. Most of them are based on the so-called distributed multipole analysis which requires assuming more or less arbitrary distribution of the multipole moments in the interacting molecules and neglects the charge overlap effects. In contrast, the symmetry-adapted perturbation theory defines the electrostatic energy without ambiguities using an exact description of the charge distributions in molecules and fully accounting for the penetration effects.

The first-order polarization energy in the symmetry-adapted perturbation theory is given by Eq. (42). For our purposes it is convenient to introduce the following representation of the intermolecular interaction operator  $V$

$$V = \sum_{i \in A} \sum_{j \in B} v(ij), \quad (49)$$

where the generalized interaction potential  $v(ij)$  is defined by [36]

$$v(ij) = r_{ij}^{-1} + v_B(i)/N_B + v_A(j)/N_A + V_0/N_A N_B. \quad (50)$$

The expression for  $E_{pol}^{(1)}$  can be rewritten as

$$E_{pol}^{(1)} = \int \rho_A(i) v(ij) \rho_B(j) d\tau_i d\tau_j, \quad (51)$$

where  $\rho_X(i)$  is the electron density of the monomer X, defined by

$$\rho_X(i) = N_X \int \Psi_X^*(1, \dots, i, \dots, N_X) \Psi_X(1, \dots, i, \dots, N_X) d\tau'_i. \quad (52)$$

The notation  $d\tau'_i$  means here that the integration is performed over all but the  $i$ th space and spin coordinates of electrons. The expression (51) clearly shows that the first-order polarization energy  $E_{pol}^{(1)}$  can be interpreted as the energy of the electrostatic interaction of unperturbed charge distributions of the isolated monomers. Equation (51) forms a convenient starting point for a perturbation expansion of

$E_{pol}^{(1)}$  in terms of the correlation operators  $W_A$  and  $W_B$ . The electron density can be expanded as a many-body series of the form

$$\rho_X(i) = \sum_{k=0}^{\infty} \lambda_X^k \rho_X^{(k)}(i), \quad (53)$$

where  $\lambda_X$  is a formal expansion parameter set later equal to 1. Substitution of the expansion (53) for the monomer A and B into Eq. (51) defines the corrections

$$E_{pol}^{(1nm)} = \int \rho_A^{(n)}(i) v(ij) \rho_B^{(m)}(j) d\tau_i d\tau_j. \quad (54)$$

The simplest way of defining the corrections  $\rho_X^{(k)}(i)$  in the many-body expansion of the electron density is based on the Møller-Plesset expansion of the wave function  $\Psi_X$  [47]

$$\Psi_X = \sum_{k=0}^{\infty} \lambda_X^k \Psi_X^{(k)}. \quad (55)$$

and leads to the following expression for the corrections  $\rho_X^{(k)}(i)$

$$\rho_X^{(k)}(i) = N_X \sum_{l=0}^k \int \Psi_X^{*(l)}(1, \dots, i, \dots, N_X) \Psi_X^{(k-l)}(1, \dots, i, \dots, N_X) d\tau_i^l. \quad (56)$$

It is possible to introduce another way of defining the corrections  $\rho_X^{(k)}(i)$  [53, 54, 55, 56] in the expansion (53). We note first that the electron density can be written as the expectation value of the operator

$$\Delta = \sum_{i=1}^{N_X} \delta(\mathbf{r} - \mathbf{r}_i), \quad (57)$$

where  $\mathbf{r}_i$  denotes the space and spin coordinate of the  $i$ th electron, and  $\mathbf{r}$  is an arbitrary position vector. In view of the Hellmann-Feynman theorem we can transform Eq. (52) to

$$\rho_X(\mathbf{r}) = \left( \frac{\partial \mathcal{E}_X(\xi; \mathbf{r})}{\partial \xi} \right)_{\xi=0}, \quad (58)$$

where  $\mathcal{E}_X(\xi; \mathbf{r})$  is the lowest eigenvalue of the hamiltonian

$$\mathcal{H}_X = H_X + \xi \sum_{i=1}^{N_X} \delta(\mathbf{r} - \mathbf{r}_i). \quad (59)$$

Introducing the Møller-Plesset parametrization of the Hamiltonian  $\mathcal{H}_X$

$$\mathcal{H}_X = \mathcal{F}_X(\xi) + \lambda_X \tilde{W}_X, \quad (60)$$

with  $\mathcal{F}_X(\xi) = \tilde{F}_X + \xi \sum_{i=1}^{N_X} \delta(\mathbf{r} - \mathbf{r}_i)$ , the perturbation-dependent energy  $\mathcal{E}_X(\xi; \mathbf{r})$  can be expanded as a power series in  $\lambda_X$

$$\mathcal{E}_X(\xi; \mathbf{r}) = \sum_{k=0} \lambda_X^k \mathcal{E}_X^{(k)}(\xi; \mathbf{r}). \quad (61)$$

[Note, that the operators  $\tilde{F}_X$  and  $\tilde{W}_X$  differ from the standard operators  $F_X$  and  $W_X$  of Eqs. (10)-(11) since the orbitals depend now on the perturbation parameter  $\xi$ .] Inserting Eq. (61) into the Eq. (58) we obtain a new many-body expansion of the electron density

$$\rho_1^X(i) = \sum_{k=0}^{\infty} \lambda_X^k \tilde{\rho}_X^{(k)}(i), \quad (62)$$

where the consecutive corrections  $\tilde{\rho}_X^{(k)}$  are given by

$$\tilde{\rho}_X^{(k)}(\mathbf{r}) = \left( \frac{\partial \mathcal{E}_X^{(k)}(\xi; \mathbf{r})}{\partial \xi} \right)_{\xi=0}. \quad (63)$$

Since the MBPT wave functions do not fulfill the Hellmann-Feynman theorem, the MBPT corrections defined by Eqs. (56) and (63) will differ in each order of MBPT. Only in the zeroth-order the two approaches lead to the same result, but this is a simple consequence of the fact that the Hartree-Fock wave function is fully variational and fulfills the Hellmann-Feynman theorem. The correlation corrections to the Hartree-Fock electron density of Eq. (56) will be referred to as non-relaxed corrections, in contrast to those defined by Eq. (63) which will be referred to as relaxed or including the orbital relaxation (response) effects [53, 54, 55, 56]. Thus, the use of different correlation corrections in Eq. (54) will lead to different expressions for  $E_{pol}^{(1nm)}$ . The corrections computed using the standard Møller-Plesset expansion of the electron density based on Eq. (56) will be simply denoted by  $E_{pol}^{(1nm)}$ . The corrections involving the MBPT expansion of the electron density based on Eq. (63) will be denoted by  $E_{pol,resp}^{(1nm)}$ . The subscript *resp* means that  $E_{pol,resp}^{(1nm)}$  includes the so called response, or orbital relaxation effects [53, 54, 55, 56]. For large intermonomer distances  $R$  and for the interaction polar molecules the two corrections behave like

$$E_{pol}^{(1nm)} \sim \frac{\mu_A^{(n)} \mu_B^{(m)}}{R^3}, \quad (64)$$

$$E_{pol,resp}^{(1nm)} \sim \frac{\tilde{\mu}_A^{(n)} \tilde{\mu}_B^{(m)}}{R^3}, \quad (65)$$

where  $\mu_X^{(n)}$  and  $\tilde{\mu}_X^{(n)}$  denote the  $n$ th-order correlation correction to the dipole moment of the monomer X in the double perturbation theory [47] and in the finite-field MBPT approach [56], respectively.

The theory presented above has been introduced in Refs. [32, 57, 58] and applied through the fourth-order in  $W_A$  and  $W_B$ . Below, we report the final orbital expressions for the corrections  $E_{pol}^{(1n0)}$  for  $n = 0, 2$ , and  $3$ , and for  $E_{pol,resp}^{(1n0)}$  for  $n = 2, 3, 4$ . At present we are working on the computer implementation of the correction  $E_{pol}^{(140)}$ .

The second-order correlation correction including the orbital relaxation (or response) effects has been introduced in Refs. [57, 59] to supplement an approximate SAPT analysis of the second-order supermolecular MBPT (MBPT(2)) energies of Chalasinski and Szczesniak [60]. Recently, the analysis of Refs. [60, 59] has been generalized [61] using a coupled cluster ansatz based on the so-called Hartree-Hartree-Fock (HHF) [62] reference state, and it can be shown that for the interaction of polar species, the supermolecular MBPT( $n$ ) energy,  $n = 2, 3, 4$ , behave at large intermonomer distances like the sum  $E_{pol,resp}^{(1n0)} + E_{pol,resp}^{(10n)}$ . For further details we refer the reader to Refs. [60, 57, 59, 61].

### 3.1 Hartree-Fock electrostatic energy $E_{pol}^{(10)}$

When the intramonomer correlation is neglected, the electrostatic energy  $E_{pol}^{(1)}$  is approximated by  $E_{pol}^{(10)}$ . Note, that the Hartree-Fock wave function is fully variational and fulfills the Hellmann-Feynman theorem. Thus, we have

$$E_{pol}^{(100)} = E_{pol,resp}^{(100)}.$$

Substituting the expression for the zeroth-order electron density into Eq. (54) we obtain

$$E_{pol}^{(100)} = 4\tilde{v}_{ab}^{ab}, \quad (66)$$

where the generalized two-electron integrals  $\tilde{v}_{ij}^{kl}$  are given by

$$\tilde{v}_{ij}^{kl} = v_{ij}^{kl} + (v_A)_j^l \delta_i^k / N_A + (v_B)_i^k \delta_j^l / N_B + \delta_i^k \delta_j^l V_0 / (N_A N_B) \quad (67)$$

The expression (66) has a particularly simple form, so the Hartree-Fock electrostatic energy can easily be calculated for large polyatomic molecules.

### 3.2 Second-order intramonomer correlation corrections

The first-order intramonomer correlation corrections  $E_{pol}^{(110)}$ ,  $E_{pol}^{(101)}$ ,  $E_{pol,resp}^{(110)}$ , and  $E_{pol,resp}^{(101)}$ , as well as the bilinear terms  $E_{pol}^{(111)}$  and  $E_{pol,resp}^{(111)}$  vanish on account of the Brillouin theorem. Thus, the leading terms in the many-body expansions of the electrostatic energy are given by the sum of  $E_{pol}^{(120)}$  and  $E_{pol}^{(102)}$ , or  $E_{pol,resp}^{(120)}$  and  $E_{pol,resp}^{(102)}$ . Since the appropriate expression for  $E_{pol}^{(102)}$  ( $E_{pol,resp}^{(102)}$ ) is obtained from the expression for  $E_{pol}^{(120)}$  ( $E_{pol,resp}^{(120)}$ ) by interchanging symbols pertaining to molecules A and B, below we consider only the corrections  $E_{pol}^{(120)}$  and  $E_{pol,resp}^{(120)}$ .

The detailed derivation of the expression for the second-order non-relaxed correction  $E_{pol}^{(120)}$  can be found in Refs. [32, 58]. The orbital formula for  $E_{pol}^{(120)}$  can be written as

$$E_{pol}^{(120)} = 4\text{Re}(\omega_B)_a^r t_r^a + 2(2t_{rr'}^{aa'} - t_{rr'}^{a'a}) (\omega_B)_{r''}^{r'} t_{aa'}^{rr''} - 2(2t_{rr'}^{aa'} - t_{rr'}^{a'a}) (\omega_B)_{a'}^{a''} t_{aa''}^{rr'} , \quad (68)$$

where  $(\omega_B)_k^l$  denotes a matrix element of the complete electrostatic potential  $\omega_B$  of molecule B calculated using the HF density matrix

$$\omega_B(\mathbf{r}) = v_B(\mathbf{r}) + 2 \sum_b \int \frac{\phi_b^*(\mathbf{r}') \phi_b(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' ,$$

whereas the first-order spin-free double excitation cluster amplitude  $t_{rr'}^{aa'}$ , and the second-order spin-free single excitation amplitude  $t_r^a$  are given by

$$t_{rr'}^{aa'} = v_{rr'}^{aa'} / \epsilon_{rr'}^{aa'} , \quad (69)$$

and

$$t_r^a = [(2t_{r''r'}^{a''a'} - t_{r''r'}^{aa''}) v_{a''r}^{r''r'} - (2t_{r''r}^{a''a'} - t_{r''r}^{a'a''}) v_{a''a'}^{r''r}] / \epsilon_r^a , \quad (70)$$

respectively. From now on, we will assume that the indices  $aa'...$  ( $rr'...$ ) are used exclusively for the occupied (virtual) orbitals of the molecule A while the indices  $bb'...$  ( $ss'...$ ) label the occupied (virtual) orbitals of the molecule B.

The expression for the relaxed correction  $E_{pol,resp}^{(120)}$  in terms of molecular integrals and cluster amplitudes has been derived in Refs. [57, 58], and is given by

$$E_{pol,resp}^{(120)} = 2(2t_{rr'}^{aa'} - t_{rr'}^{a'a})(\omega_B)_{r''}^{r'} t_{aa''}^{rr''} - 2(2t_{rr'}^{aa'} - t_{rr'}^{a'a})(\omega_B)_{a''}^{a'} t_{aa''}^{rr''} + 4\text{Re } Y_r^{(2)a} C_a^r, \quad (71)$$

where  $C_r^a$  are the spin-free Coupled-Perturbed Hartree-Fock (CPHF) coefficients [63] which fulfill the following set of equations

$$(\epsilon_r - \epsilon_a)C_r^a + (2v_{ra'}^{ar'} - v_{ra'}^{r'a})C_{r'}^{a'} + (2v_{rr'}^{aa'} - v_{rr'}^{a'a})C_{a'}^{r'} + (\omega_B)_r^a = 0. \quad (72)$$

and  $Y_r^{(2)a}$  is given by

$$\begin{aligned} Y_r^{(2)a} = & (2t_{r_1 r'}^{a_1 a'} - t_{r_1 r'}^{a' a_1}) t_{a_1 a'}^{r_1 r''} (2v_{rr''}^{ar'} - v_{rr''}^{r'a}) - (2t_{r_1 r'}^{a_1 a'} - t_{r_1 r'}^{a' a_1}) t_{a_1 a''}^{r_1 r'} (2v_{ra''}^{aa'} - v_{ra''}^{a'a}) + \\ & + (2t_{r'' r'}^{a'' a} - t_{r'' r'}^{aa''}) v_{a'' r}^{r'' r'} - (2t_{r'' r}^{a'' a'} - t_{r'' r}^{a' a''}) v_{a'' a'}^{r'' a}. \end{aligned} \quad (73)$$

It is not difficult to show [57, 58] that the second-order correction including orbital response  $E_{pol,resp}^{(120)}$  is in fact of infinite-order in  $W_A$ . Using the perturbation expansion of the CPHF coefficients, defined recursively by

$$\bar{C}_r^{(0)a} = (\omega_B)_r^a / \epsilon_r^a, \quad (74)$$

$$\bar{C}_r^{(n+1)a} = [(2v_{ra'}^{ar'} - v_{ra'}^{r'a}) \bar{C}_r^{(n)a} + (2v_{rr'}^{aa'} - v_{rr'}^{a'a}) \bar{C}_a^{(n)r}] / \epsilon_r^a, \quad (75)$$

one can prove that the difference  $E_{pol,resp}^{(120)} - E_{pol}^{(120)}$  is given by

$$\begin{aligned} E_{pol,resp}^{(120)} - E_{pol}^{(120)} = & 4\text{Re}(2t_{r_1 r'}^{a_1 a'} - t_{r_1 r'}^{a' a_1}) t_{a_1 a'}^{r_1 r''} (2v_{rr''}^{ar'} - v_{rr''}^{r'a}) \bar{C}_a^{(0)r} + \\ & - 4\text{Re}(2t_{r_1 r'}^{a_1 a'} - t_{r_1 r'}^{a' a_1}) t_{a_1 a''}^{r_1 r'} (2v_{ra''}^{aa'} - v_{ra''}^{a'a}) \bar{C}_a^{(0)r} + 4\text{Re} \sum_{n=1}^{\infty} Y_r^{(2)a} \bar{C}_a^{(n)r}. \end{aligned} \quad (76)$$

Thus, the correction  $E_{pol,resp}^{(120)}$  and higher-order corrections including the orbital relaxation effects sum up to infinity certain diagrams appearing in higher-orders of the many-body expansion of the electrostatic energy based on non-relaxed density matrices.

### 3.3 Third-order intramonomer correlation corrections

The bilinear terms  $E_{pol}^{(121)}$ ,  $E_{pol}^{(112)}$ ,  $E_{pol,resp}^{(121)}$ , and  $E_{pol,resp}^{(112)}$  vanish on account of the Brillouin theorem, so the third-order corrections in the many-body expansions of the electrostatic energy are given by the sum of  $E_{pol}^{(130)}$  and  $E_{pol}^{(103)}$ , or  $E_{pol,resp}^{(130)}$  and  $E_{pol,resp}^{(103)}$ . Since the appropriate expression for  $E_{pol}^{(103)}$  ( $E_{pol,resp}^{(103)}$ ) is obtained from the expression for  $E_{pol}^{(130)}$  ( $E_{pol,resp}^{(130)}$ ) by interchanging symbols pertaining to molecules A and B, below we consider only the corrections  $E_{pol}^{(130)}$  and  $E_{pol,resp}^{(130)}$ .

The expression for the non-relaxed third-order correction is somewhat more involved and can be written as [58]

$$E_{pol}^{(130)} = 4\text{Re}(\bar{Z}_r^a(\omega_B)_a^r + (2 \stackrel{(2)}{t}_{rr''}^{aa''} - \stackrel{(2)}{t}_{rr''}^{a''a})t_{aa''}^{r'r''}(\omega_B)_{r'}^r - (2 \stackrel{(2)}{t}_{r'r''}^{a'a''} - \stackrel{(2)}{t}_{r'r''}^{a''a'})t_{aa''}^{r'r''}(\omega_B)_{a'}^a), \quad (77)$$

where the second-order spin-free double excitation cluster amplitude  $\stackrel{(2)}{t}_{rr''}^{aa'}$  is given by

$$\begin{aligned} \stackrel{(2)}{t}_{rr''}^{aa'} = & [(v_{rr''}^{r'r'''} t_{rr''}^{aa'} + v_{aa''}^{a'a'''} t_{rr''}^{aa''} + v_{r'r''}^{a'r'''}(2t_{rr''}^{aa''} - t_{rr''}^{a''a}) + \\ & + v_{ra''}^{ar'''}(2t_{r'r''}^{a'a''} - t_{r'r''}^{a''a'}) - v_{aa''}^{a'r'''} t_{rr''}^{aa''} - v_{aa''}^{ar'''} t_{r'r''}^{a'a''} - v_{aa''}^{a'r''} t_{rr''}^{a'a'} - v_{aa''}^{r'r''} t_{r'r''}^{a'a''}]/\epsilon_{rr''}^{aa'}, \end{aligned} \quad (78)$$

and  $\bar{Z}_r^a$  is defined by

$$\begin{aligned} \bar{Z}_r^a = & [(2 \stackrel{(2)}{t}_{r'r''}^{a''a} - \stackrel{(2)}{t}_{r'r''}^{aa''})v_{aa''}^{r'r'} - (2 \stackrel{(2)}{t}_{r'r''}^{a''a'} - \stackrel{(2)}{t}_{r'r''}^{a'a''})v_{aa''}^{r'a'} + t_{r'}^{a'}(2v_{aa''}^{r'a} - v_{aa''}^{ar'}) + \\ & + t_{a'}^{r'}(2v_{rr''}^{aa'} - v_{rr''}^{a'a}) + (2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1})t_{a_1a'}^{r_1r''}(2v_{rr''}^{ar'} - v_{rr''}^{r'a}) - (2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1})t_{a_1a''}^{r_1r'}(2v_{ra''}^{aa''} - v_{ra''}^{a''a}) + \\ & + \bar{\gamma}_{a_1a''}^{(2)a'a''}(2v_{ra''}^{a_1a''} - v_{ra''}^{a''a_1}) + \bar{\gamma}_{r_1r''}^{(2)r_1r''}(2v_{rr''}^{ar'} - v_{rr''}^{r'a}) + \bar{\gamma}_{r'a'}^{(2)ar''}(2v_{r'r''}^{a''r'} - v_{r'r''}^{r'a''}) + \\ & - \bar{\gamma}_{r'a'}^{(2)ar''}(2v_{r'r''}^{r'a''} - v_{r'r''}^{a''r'}) - \bar{\gamma}_{ra''}^{(2)a'r''}(2v_{aa''}^{a'r''} - v_{aa''}^{r'a''}) + \bar{\gamma}_{ra''}^{(2)a'r''}(2v_{aa''}^{a''r'} - v_{aa''}^{r'a''})]/\epsilon_r^a. \end{aligned} \quad (79)$$

Finally, the intermediate quantities  $\bar{\gamma}_{a_1a''}^{(2)a'a''}$ ,  $\bar{\gamma}_{r_1r''}^{(2)r_1r''}$ ,  $\bar{\gamma}_{ra''}^{(2)ar'}$  and  $\bar{\gamma}_{ra''}^{(2)ar'}$  are defined as

$$\bar{\gamma}_{r_1r''}^{(2)r_1r''} = t_{aa''}^{r_1r''} t_{rr''}^{aa'}, \quad (80)$$

$$\bar{\gamma}_{a_1a''}^{(2)a'a''} = t_{a_1a''}^{rr'} t_{rr''}^{aa'}, \quad (81)$$

$$\bar{\gamma}_{ra''}^{(2)ar'} = (2t_{rr''}^{aa''} - t_{rr''}^{a''a})t_{aa''}^{r'r'} - t_{rr''}^{aa''} t_{aa''}^{r'r'}, \quad (82)$$

$$\bar{\gamma}_{ra''}^{(2)ar'} = t_{rr''}^{a''a} t_{aa''}^{r'r'}. \quad (83)$$

The expansion of the third-order relaxed correction  $E_{pol,resp}^{(130)}$  in terms of molecular integrals and cluster amplitudes has been done in Ref. [58]. The result of this expansion is

$$E_{pol,resp}^{(130)} = 4\text{Re}(Y_r^a C_a^r + (2 \overset{(2)}{t}_{rr''}^{aa''} - \overset{(2)}{t}_{rr''}^{a''a}) t_{a'a''}^{r'r''} (\omega_B)_{r'}^r - (2 \overset{(2)}{t}_{r'r''}^{a'a''} - \overset{(2)}{t}_{r'r''}^{a''a'}) t_{aa''}^{r'r''} (\omega_B)_{a'}^a), \quad (84)$$

where  $Y_r^a$  is given by

$$\begin{aligned} Y_r^a = & (2 \overset{(2)}{t}_{r'r''}^{a''a} - \overset{(2)}{t}_{r'r''}^{aa''}) v_{a''r}^{r'r'} - (2 \overset{(2)}{t}_{r''r}^{a''a} - \overset{(2)}{t}_{r''r}^{aa''}) v_{a''a'}^{r''r'} + \\ & + (2 \overset{(2)}{t}_{r_1r'}^{a_1a'} - \overset{(2)}{t}_{r_1r'}^{a'a_1}) t_{a_1a'}^{r_1r''} (2v_{rr''}^{ar'} - v_{rr''}^{r'a}) + (2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1}) \overset{(2)}{t}_{a_1a'}^{r_1r''} (2v_{rr''}^{ar'} - v_{rr''}^{r'a}) + \\ & - (2 \overset{(2)}{t}_{r_1r'}^{a_1a'} - \overset{(2)}{t}_{r_1r'}^{a'a_1}) t_{a_1a''}^{r_1r'} (2v_{ra'}^{aa''} - v_{ra'}^{a''a}) - (2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1}) \overset{(2)}{t}_{a_1a''}^{r_1r'} (2v_{ra'}^{aa''} - v_{ra'}^{a''a}) + \\ & + \overset{(2)}{\gamma}_{a_1a''}^a (2v_{ra'}^{a_1a''} - v_{ra'}^{a''a_1}) + \overset{(2)}{\gamma}_{r_1r''}^{r_1r''} (2v_{r_1r''}^{ar'} - v_{r_1r''}^{r'a}) + \overset{(2)}{\gamma}_{r'a'}^{ar''} (2v_{r''r}^{a''r'} - v_{r''r}^{r'a''}) + \\ & - \overset{(2)}{\gamma}_{r'a''}^{ar''} (2v_{r''r}^{r'a''} - v_{r''r}^{a''r'}) - \overset{(2)}{\gamma}_{ra''}^{a'r''} (2v_{a'r''}^{aa''} - v_{a'r''}^{a''a}) + \overset{(2)}{\gamma}_{ra''}^{a'r''} (2v_{a'r''}^{a''a} - v_{a'r''}^{aa''}), \quad (85) \end{aligned}$$

and  $\gamma$ 's are defined by Eqs. (80)-(83).

The comparison of the corrections  $E_{pol}^{(130)}$  and  $E_{pol,resp}^{(130)}$  is more complicated since the third-order non-relaxed correction sums certain diagrams entering the expression for  $E_{pol,resp}^{(120)}$ . Using the perturbation expansion of the CPHF coefficients defined by Eqs. (74)-(75) it can be shown [58] that

$$\begin{aligned} E_{pol,resp}^{(130)} - E_{pol}^{(130)} = & 4\text{Re}[(2 \overset{(2)}{t}_{r_1r'}^{a_1a'} - \overset{(2)}{t}_{r_1r'}^{a'a_1}) t_{a_1a'}^{r_1r''} (2v_{rr''}^{ar'} - v_{rr''}^{r'a}) \overset{(0)}{C}_a^r + \\ & + (2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1}) \overset{(2)}{t}_{a_1a'}^{r_1r''} (2v_{rr''}^{ar'} - v_{rr''}^{r'a}) \overset{(0)}{C}_a^r - (2 \overset{(2)}{t}_{r_1r'}^{a_1a'} - \overset{(2)}{t}_{r_1r'}^{a'a_1}) t_{a_1a''}^{r_1r'} (2v_{ra'}^{aa''} - v_{ra'}^{a''a}) \overset{(0)}{C}_a^r + \\ & - (2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1}) \overset{(2)}{t}_{a_1a''}^{r_1r'} (2v_{ra'}^{aa''} - v_{ra'}^{a''a}) \overset{(0)}{C}_a^r + \sum_{n=1}^{\infty} \overset{(3)}{Y}_r^a \overset{(n)}{C}_a^r] - D1 - D2 - D3, \quad (86) \end{aligned}$$

where  $D1$ ,  $D2$ , and  $D3$  are the third-order terms of Eq. (76). Note, that in contrast to the second-order correction  $E_{pol,resp}^{(120)}$ ,  $E_{pol,resp}^{(130)}$  does not contain all diagrams included in  $E_{pol}^{(130)}$ , since it is missing terms denoted in Eq. (86) by  $D1$ ,  $D2$ , and  $D3$  which are already included in  $E_{pol,resp}^{(120)}$ .



### 3.4 Fourth-order intramonomer correlation corrections

The bilinear terms  $E_{pol}^{(121)}$ ,  $E_{pol}^{(112)}$ ,  $E_{pol,resp}^{(121)}$ , and  $E_{pol,resp}^{(112)}$  vanish on account of the Brillouin theorem, so the fourth-order corrections in the many-body expansions of the electrostatic energy are given by the sum of quartic terms  $E_{pol}^{(140)}$  and  $E_{pol}^{(104)}$ , or  $E_{pol,resp}^{(140)}$  and  $E_{pol,resp}^{(104)}$ , and of bilinear terms  $E_{pol}^{(122)}$  or  $E_{pol,resp}^{(122)}$ . In this section we consider only the correction  $E_{pol,resp}^{(140)}$ . At present we are working on the computer implementation of  $E_{pol}^{(140)}$ . It can be shown that the bilinear term  $E_{pol}^{(122)}$  ( $E_{pol,resp}^{(122)}$ ) appears in the MBPT5 (and higher order) supermolecular interaction energy, and therefore, it will not be considered here. Since the appropriate expression for  $E_{pol,resp}^{(104)}$  is obtained from the expression for  $E_{pol,resp}^{(140)}$  by interchanging symbols pertaining to molecules A and B, below we consider only the relaxed correction  $E_{pol,resp}^{(140)}$ .

The expression for the fourth-order correction  $E_{pol,resp}^{(140)}$  can be written as [58]

$$E_{pol,resp}^{(140)} = (\omega_B)_a^{a'} \rho_a^{(4)a} + (\omega_B)_r^{r'} \rho_r^{(4)r} + 4\text{Re } Y_r^a C_a^r, \quad (87)$$

where  $\rho_a^{(4)a'}$ ,  $\rho_r^{(4)r'}$ , and  $Y_r^a$  are given by

$$\begin{aligned} \rho_a^{(4)a'} = & -2t_r^{a'} t_a^r - (2 t_{r'r''}^{a'a''} - t_{r'r''}^{a''a'}) (t_{aa''}^{r'r''} + \Lambda_{aa''}^{r'r''}) - (2 t_{r'r''}^{a'a''} - t_{r'r''}^{a''a'}) t_{aa''}^{r'r''} + \\ & -(2t_{r'r''}^{a'a''} - t_{r'r''}^{a''a'}) (t_{aa''}^{r'r''} + \Lambda_{aa''}^{r'r''}) - (2 t_{r'r''}^{a'a''} - t_{r'r''}^{a''a'}) t_{aa''}^{r'r''} + \\ & -\frac{1}{2} t_{aa''}^{rr'r_1} [4t_{rr'r_1}^{a'a_1a_2} + t_{rr'r_1}^{a'a_1a_2} + t_{r_1rr'}^{a'a_1a_2} - 2(t_{rr'r_1}^{a'a_1a_2} + t_{r_1rr'}^{a'a_1a_2} + t_{rr'r_1}^{a'a_1a_2})], \end{aligned} \quad (88)$$

$$\begin{aligned} \rho_r^{(4)r'} = & 2t_r^a t_a^{r'} + 2(2 t_{rr''}^{aa''} - t_{rr''}^{a''a'}) (t_{aa''}^{r'r''} + \Lambda_{aa''}^{r'r''}) + \\ & + 2(2t_{rr''}^{aa''} - t_{rr''}^{a''a'}) (t_{aa''}^{r'r''} + \Lambda_{aa''}^{r'r''}) + 2(2 t_{rr''}^{aa''} - t_{rr''}^{a''a'}) t_{aa''}^{r'r''} + \\ & + \frac{1}{2} t_{aa''}^{rr'r_1} [4t_{rr'r_1}^{aa'a_1} + t_{rr'r_1}^{aa'a_1} + t_{rr'r_1}^{aa'a_1} - 2(t_{rr'r_1}^{aa'a_1} + t_{rr'r_1}^{aa'a_1} + t_{rr'r_1}^{aa'a_1})], \end{aligned} \quad (89)$$

$$\begin{aligned} Y_r^a = & \rho_{a'}^{(4)a''} (2v_{a''r}^{a'a} - v_{a''r}^{aa'}) + \rho_{r'}^{(4)r''} (2v_{r''r}^{r'a} - v_{r''r}^{ar'}) + \\ & + (2 t_{r''r'}^{a''a'} - t_{r''r'}^{aa''} + 2 \Lambda_{r''r'}^{a''a'} - \Lambda_{r''r'}^{aa''}) v_{a''r}^{r'r'} + \\ & - (2 t_{r''r}^{a''a} - t_{r''r}^{aa''} + 2 \Lambda_{r''r}^{a''a} - \Lambda_{r''r}^{aa''}) v_{a''r}^{r'a'} + \\ & + \gamma_{a_1a''}^{(3)a'a'} (2v_{ra'}^{a_1a''} - v_{ra'}^{a''a_1}) + \gamma_{r_1r''}^{(3)r'r'} (2v_{r_1r''}^{ar'} - v_{r_1r''}^{r'a}) + \gamma_{r'a'}^{(3)ar''} (2v_{r''r}^{a''r'} - v_{r''r}^{r'a''}) + \\ & - \gamma_{r'a'}^{(3)ar''} (2v_{r''r}^{r'a''} - v_{r''r}^{a''r'}) - \gamma_{ra''}^{(3)a'r''} (2v_{a'r''}^{aa''} - v_{a'r''}^{a''a}) + \gamma_{ra''}^{(3)a'r''} (2v_{a'r''}^{a''a} - v_{a'r''}^{aa''}) + \end{aligned}$$

$$\begin{aligned}
& -\gamma_{ra_2}^{(3)r_1r_2}(2v_{r_1r_2}^{aa_2} - v_{r_1r_2}^{a_2a}) - \gamma_{rr_2}^{(3)r_1a_2}(2v_{r_1a_2}^{ar_2} - v_{r_1a_2}^{r_2a}) - \gamma_{r_2r}^{(3)r_1a_2}(2v_{r_1a_2}^{r_2a} - v_{r_1a_2}^{ar_2}) + \\
& + \gamma_{rr_1}^{(3)r_1a}(2v_{rr_1}^{r_2r'} - v_{rr_1}^{r'r_2}) - \gamma_{a_1a_2}^{(3)ar'}(2v_{rr'}^{a_1a_2} - v_{rr'}^{a_2a_1}) - \gamma_{a'r_1}^{(3)aa_1}(2v_{ra_1}^{a'r_1} - v_{ra_1}^{r_1a}) + \\
& - \gamma_{a'r_1}^{(3)a_1a}(2v_{ra_1}^{r_1a'} - v_{ra_1}^{a'r_1}) + \gamma_{a'r}^{(3)a_1a_2}(2v_{a_1a_2}^{a'a} - v_{a_1a_2}^{aa'}). \tag{90}
\end{aligned}$$

The spin-free triple excitation amplitudes are defined as in Refs. [66, 67]. Specifically, the second-order spin-free triple excitation amplitude  $t_{rr_1r_2}^{aa_1a_2}$  can be written as

$$\begin{aligned}
t_{rr_1r_2}^{aa_1a_2} = & [v_{rr_1}^{ar'}t_{r_2r'}^{a_2a_1} + v_{r_1r}^{a_1r'}t_{r_2r'}^{a_2a} + v_{r_2r}^{a_2r'}t_{r_1r'}^{a_1a} + v_{rr_2}^{ar'}t_{r_1r'}^{a_1a_2} + v_{r_2r_1}^{a_2r'}t_{rr'}^{aa_1} + v_{r_1r_2}^{a_1r'}t_{rr'}^{aa_2} + \\
& - v_{ra'}^{aa_1}t_{r_1r_2}^{a'a_2} - v_{r_1a'}^{a_1a}t_{rr_2}^{a'a_2} - v_{r_2a'}^{a_2a}t_{rr_1}^{a'a_1} - v_{ra'}^{aa_2}t_{r_2r_1}^{a'a_1} - v_{r_2a'}^{a_2a_1}t_{r_1r}^{a'a} - v_{r_1a'}^{a_1a_2}t_{r_2r}^{a'a}]/\epsilon_{rr_1r_2}^{aa_1a_2}.
\end{aligned}$$

The spin-free third-order double excitation amplitude  $t_{rr'}^{aa'}$  separates into contributions which originate from single, double, triple, and quadruple excitations

$$t_{rr'}^{aa'} = t_{rr'}^{aa'}(S) + t_{rr'}^{aa'}(D) + t_{rr'}^{aa'}(T) + t_{rr'}^{aa'}(Q).$$

The specific expressions for these contributions are

$$\begin{aligned}
t_{rr'}^{aa'}(S) = & [v_{rr'}^{r_1a'}t_{r_1}^a + v_{r'r}^{r_1a}t_{r_1}^{a'} - v_{a_1r'}^{aa'}t_{r_1}^{a_1} - v_{a_1r}^{a'a}t_{r_1}^{a_1}]/\epsilon_{rr'}^{aa'}, \\
t_{rr'}^{aa'}(D) = & [v_{rr'}^{r''r'''}t_{r''r'''}^{aa'} + v_{a''a'''}^{aa'}t_{r''r'''}^{a''a'''} + v_{r''a'''}^{a'r''}(2t_{rr''}^{aa''} - t_{rr''}^{a''a}) + \\
& + v_{ra'''}^{ar''}(2t_{r'r''}^{a'a''} - t_{r'r''}^{a''a'}) - v_{a''r'}^{a'r''}t_{rr''}^{aa''} - v_{a''r}^{ar''}t_{r'r''}^{a'a''} - v_{a''r'}^{a'r''}t_{r'r''}^{a''a'} - v_{a''r}^{ar''}t_{r'r''}^{a''a'}]/\epsilon_{rr'}^{aa'}, \\
t_{rr'}^{aa'}(T) = & [v_{ra_1}^{r_2r_1}(2t_{r'r_1r_2}^{a'a_1a} - t_{r'r_1r_2}^{a_1a'a} - t_{r'r_1r_2}^{aa_1a'}) + v_{r'a_1}^{r_2r_1}(2t_{rr_1r_2}^{aa_1a'} - t_{rr_1r_2}^{a_1aa'} - t_{rr_1r_2}^{a'a_1a}) + \\
& - v_{a_2a_1}^{ar_1}(2t_{rr'r_1}^{a_1a'a_2} - t_{rr'r_1}^{a_1a'a_2} - t_{r_1r'r}^{a_1a'a_2}) - v_{a_2a_1}^{a'r_1}(2t_{r'r_1r_1}^{a_1aa_2} - t_{r'r_1r_1}^{a_1aa_2} - t_{r_1r'r_1}^{a_1aa_2})]/\epsilon_{rr'}^{aa'}, \\
t_{rr'}^{aa'}(Q) = & [v_{a_1a_2}^{r_1r_2}t_{r_1r_2}^{aa'}t_{rr'}^{a_1a_2} + (2v_{a_1a_2}^{r_1r_2} - v_{a_1a_2}^{r_2r_1})t_{rr_2}^{aa_2}(2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1}) + \\
& - v_{a_1a_2}^{r_1r_2}t_{rr_2}^{a_2a}(2t_{r_1r'}^{a_1a'} - t_{r_1r'}^{a'a_1}) + v_{a_1a_2}^{r_2r_1}t_{rr_2}^{a_2a}t_{r_1r'}^{a_1a'}v_{a_1a_2}^{r_2r_1}t_{rr_2}^{a_2a'}t_{r'r_1}^{a_1a} + \\
& - (2v_{a_1a_2}^{r_1r_2} - v_{a_1a_2}^{r_2r_1})t_{rr_2}^{a_1a_2}t_{r_1r'}^{aa'} - (2v_{a_1a_2}^{r_1r_2} - v_{a_1a_2}^{r_2r_1})t_{r_1r_2}^{aa_2}t_{rr'}^{a_1a'} + \\
& - (2v_{a_1a_2}^{r_1r_2} - v_{a_1a_2}^{r_2r_1})t_{r'r_2}^{a_1a_2}t_{r_1r}^{a'a} - (2v_{a_1a_2}^{r_1r_2} - v_{a_1a_2}^{r_2r_1})t_{r_1r_2}^{a'a_2}t_{r'r}^{a_1a}]/\epsilon_{rr'}^{aa'}.
\end{aligned}$$

It can be shown that the amplitude  $\Lambda_{rr'}^{aa'}$  can be written as

$$\Lambda_{rr'}^{aa'} = \frac{1}{12} < (2E_{rr'}^{aa'} + E_{rr'}^{a'a})[[T_{20}^{\dagger(010)}, T_{20}^{(010)}], T_{20}^{(010)}] >, \tag{91}$$

where  $E_{rr'}^{aa'}$  is the orbital replacement operator [64, 65]. Applying the spin-free Wick theorem [65] to the expression (91) we obtain the following orbital formula for  $\Lambda_{rr'}^{(3)aa'}$

$$\begin{aligned} \Lambda_{rr'}^{(3)aa'} = & t_{a_1 a_2}^{r_1 r_2} t_{r_1 r_2}^{aa'} t_{rr'}^{a_1 a_2} + (2t_{a_1 a_2}^{r_1 r_2} - t_{a_1 a_2}^{r_2 r_1}) t_{rr_2}^{aa_2} (2t_{r_1 r'}^{a_1 a'} - t_{r_1 r'}^{a' a_1}) + \\ & - t_{a_1 a_2}^{r_1 r_2} t_{rr_2}^{a_2 a} (2t_{r_1 r'}^{a_1 a'} - t_{r_1 r'}^{a' a_1}) + t_{a_1 a_2}^{r_2 r_1} t_{rr_2}^{a_2 a} t_{r_1 r'}^{a_1 a'} t_{a_1 a_2}^{r_2 r_1} t_{rr_2}^{a_2 a'} t_{r' r_1}^{a_1 a} + \\ & - (2t_{a_1 a_2}^{r_1 r_2} - t_{a_1 a_2}^{r_2 r_1}) t_{rr_2}^{a_1 a_2} t_{rr'}^{aa'} - (2t_{a_1 a_2}^{r_1 r_2} - t_{a_1 a_2}^{r_2 r_1}) t_{r_1 r_2}^{aa_2} t_{rr'}^{a_1 a'} + \\ & - (2t_{a_1 a_2}^{r_1 r_2} - t_{a_1 a_2}^{r_2 r_1}) t_{r' r_2}^{a_1 a_2} t_{r_1 r}^{a' a} - (2t_{a_1 a_2}^{r_1 r_2} - t_{a_1 a_2}^{r_2 r_1}) t_{r_1 r_2}^{a' a_2} t_{r' r}^{a_1 a}. \end{aligned} \quad (92)$$

Finally, the intermediate quantities appearing in Eq. (90) are defined as

$$\gamma_{r r'}^{(3)r_1 r''} = t_{aa'}^{r_1 r''} t_{rr'}^{(2)aa'} + t_{aa'}^{(2)r_1 r''} t_{rr'}^{aa'}, \quad (93)$$

$$\gamma_{a_1 a''}^{(3)a a'} = t_{a_1 a''}^{r r'} t_{rr'}^{(2)aa'} + t_{a_1 a''}^{(2)r r'} t_{rr'}^{aa'}, \quad (94)$$

$$\gamma_{ra'}^{(3)ar'} = (2t_{rr''}^{aa''} - t_{rr''}^{a'' a}) t_{a'' a'}^{r'' r'} + (2 t_{rr''}^{(2)aa''} - t_{rr''}^{(2)a'' a}) t_{a'' a'}^{r'' r'} - t_{rr''}^{aa''} t_{a'' a'}^{r'' r'} - t_{rr''}^{(2)aa''} t_{a'' a'}^{r'' r'}, \quad (95)$$

$$\gamma_{ra'}^{(3)ar'} = t_{rr''}^{a'' a} t_{a'' a'}^{r'' r'} + t_{rr''}^{aa''} t_{a'' a'}^{r'' r'}, \quad (96)$$

$$\gamma_{ra'}^{(3)r' r''} = (\gamma_{r' r''}^{(3)ra})^* = t_r^{a'} t_{a' a}^{r' r''} + t_{r' r_1}^{a' a''} (2t_{aa' a''}^{r' r'' r_1} - t_{a' a' a}^{r' r'' r_1} - t_{aa' a''}^{r' r'' r_1}), \quad (97)$$

$$\gamma_{ra}^{(3)a' a''} = (\gamma_{a' a''}^{(3)ra})^* = t_a^{r_1} t_{r_1 r}^{a' a''} + t_{a' a_1}^{r' r''} (2t_{rr' r''}^{a' a'' a_1} - t_{r'' r' r}^{a' a'' a_1} - t_{rr' r''}^{a' a'' a_1}). \quad (98)$$

## 4 First-order exchange energy

The most important short-range contribution to the interaction energy between closed-shell molecules is the exchange part of the first-order energy. This energy correction, unlike the electrostatic, induction or dispersion energies, cannot be related to any experimentally known property of the monomers, therefore *ab initio* calculations are of primary importance. It can be shown [34] that the expression for first-order exchange energy in the single exchange approximation  $E_{exch}^{(1)}(S^2)$  can be written as

$$E_{exch}^{(1)}(S^2) = \int (v(ij) - Q^{(1)}) \rho_{int}(ij) d\tau_i d\tau_j, \quad (99)$$

where  $Q^{(1)} = E_{pol}^{(1)}/N_A N_B$ , and the interaction density matrix  $\rho_{int}$  is defined as

$$\rho_{int}(ij) = \int \Psi_A^* \Psi_B^* P_1 \Psi_A \Psi_B d\tau'_{ij}. \quad (100)$$

The notation  $d\tau'_{ij}$  means here that the integration is performed over all but the  $i$ th and  $j$ th spin and space coordinates of electrons in the complex AB. Similar expression for the correction  $E_{pol}^{(1)}$  is given by Eq. (51). It is not difficult to prove that the interaction density matrix can be expressed through the one- and two-particle density matrices of the monomers

$$\begin{aligned} \rho_{int}(ij) = & -\rho_1^A(i | j)\rho_1^B(j | i) - \int \rho_2^A(ik | ij)\rho_1^B(j | k)d\tau_k + \\ & - \int \rho_1^A(i | l)\rho_2^B(jl | ji)d\tau_l - \int \rho_2^A(ik | il)\rho_2^B(jl | jk)d\tau_k d\tau_l, \end{aligned} \quad (101)$$

where the  $\rho_1^X(i | i')$  and  $\rho_2^X(ij | i'j')$  are the standard one- and two-particle density matrices of the monomer X, and are defined by

$$\rho_1^X(i | i') = N_X \int \Psi_X^*(1, \dots, i, \dots, N_X) \Psi_X(1, \dots, i', \dots, N_X) d\tau'_i, \quad (102)$$

$$\rho_2^X(ij | i'j') = N_X(N_X - 1) \int \Psi_X^*(1, \dots, i, \dots, j, \dots, N_X) \Psi_X(1, \dots, i', \dots, j', \dots, N_X) d\tau'_{ij}. \quad (103)$$

Equations (99) and (101) form a convenient starting point for a perturbation expansion of  $E_{exch}^{(1)}(S^2)$  in terms of the correlation operators  $W_A$  and  $W_B$ . The Møller-Plesset expansion of the wave function (55) defines the many-body perturbation theory expansions of the one- and two-particle density matrices

$$\rho_1^X(i | i') = \sum_{k=0}^{\infty} \lambda_X^k \rho_1^{(k)X}(i | i'), \quad (104)$$

$$\rho_2^X(ij | i'j') = \sum_{k=0}^{\infty} \lambda_X^k \rho_2^{(k)X}(ij | i'j'). \quad (105)$$

The explicit expressions for the corrections  $\rho_1^{(k)X}(i | i')$  and  $\rho_2^{(k)X}(ij | i'j')$  can be easily found by substituting the expansion (55) into Eqs. (102) and (103) and collecting coefficients at  $\lambda_X^k$ . Inserting Eqs. (104) and (105) into Eqs. (101), (100) and (51) defines an expansion of  $E_{exch}^{(1)}(S^2)$  as double power series in  $\lambda_A$  and  $\lambda_B$

$$E_{exch}^{(1)}(S^2) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda_A^n \lambda_B^m E_{exch}^{(1nm)}. \quad (106)$$

Setting  $\lambda_A = \lambda_B = 1$  we find that the first-order exchange energy is the sum of corrections  $E_{exch}^{(1nm)}$  which are of  $n$ th-order in  $W_A$  and  $m$ th-order in  $W_B$ . The explicit expression for  $E_{exch}^{(1nm)}$  is given by

$$E_{exch}^{(1nm)} = \int v(ij) \rho_{int}^{(nm)}(ij) d\tau_i d\tau_j + \sum_{k=0}^n \sum_{l=0}^m E_{pol}^{(1,n-k,m-l)} \int \rho_1^{(k)A}(i|j) \rho_1^{(l)B}(j|i) d\tau_i d\tau_j, \quad (107)$$

where

$$\begin{aligned} \rho_{int}^{(nm)}(ij) = & -\rho_1^{(n)A}(i|j) \rho_1^{(m)B}(j|i) - \int \rho_2^{(n)A}(ik|ij) \rho_1^{(m)B}(j|k) d\tau_k + \\ & - \int \rho_1^{(n)A}(i|l) \rho_2^{(m)B}(jl|ji) d\tau_l - \int \rho_2^{(n)A}(ik|il) \rho_2^{(m)B}(jl|jk) d\tau_k d\tau_l, \end{aligned} \quad (108)$$

and  $E_{pol}^{(1nm)}$  is given by Eq. (54).

The theory presented above has been introduced in Ref. [34] and applied through the second-order in  $W = W_A + W_B$ . Below, we report final orbital expressions for the corrections  $E_{exch}^{(1nm)}$ ,  $n + m \leq 2$ .

There exists an alternative approach to the exchange energy. Assuming that the orbitals of both monomers span the same linear space, the single-exchange operator acts in  $\mathcal{F}_{AB}$ , and can be put in the second-quantized form [33]

$$P_1 = -S_\kappa^\mu S_\nu^\lambda a_\lambda^\kappa b_\mu^\nu, \quad (109)$$

where  $S_\kappa^\mu$  is the overlap integral  $S_\kappa^\mu = \langle \phi_\kappa^A | \phi_\mu^B \rangle$ . Under this assumption the first-order exchange energy can be expressed in a form showing explicitly its connected and size-extensive character [33]

$$E_{exch}^{(1)}(S^2) = \sum_{(n,m) \neq (0,0)} \langle e^{-S} e^{T^\dagger} V e^{-T^\dagger} e^S | \hat{\mathcal{P}}_{nm} | e^{S^\dagger} e^{-T} P e^T e^{-S^\dagger} \rangle, \quad (110)$$

where  $T = T_A + T_B$ ,  $S = S_A + S_B$ , and  $\hat{\mathcal{P}}_{nm}$  denotes a superoperator projecting on the manifold of  $n$ -tuple excitations on monomer  $A$  and  $m$ -tuple excitations on monomer  $B$ . The operator  $S_A(S_B)$  is a cluster operator

$$S_A = \sum_{n=1}^{N_A} S_{n0},$$

and the amplitudes of  $S_{n0}$  can be obtained by solving the following set of linear equations

$$\langle a_{\alpha_1 \dots \alpha_n}^{\rho_1 \dots \rho_n} | e^{-T_A} e^{-T_A^\dagger} (Q + [Q, S_A]) e^{T_A^\dagger} e^{T_A} \rangle = 0, \quad (111)$$

where  $Q = a_\rho^\rho$ . For a detailed derivation of Eq. (111) we refer the reader to Ref. [47]. Note, that in view of Eq. (111) the operator  $S_A$  is fully determined by the operator  $T_A$ , so it can be represented as a MBPT series. Substituting the MBPT expansions of the operators  $T_A(T_B)$  and  $S_A(S_B)$  into Eq. (110), one obtains explicit formulas for the corrections  $E_{exch}^{(1nm)}$ .

It can be shown [33] that the final expressions for the corrections  $E_{exch}^{(1nm)}$  are structurally equivalent to the formulas for some polarization corrections since only Coulomb integrals appear and no additional four-index transformation of various exchange and hybrid integrals is necessary. It should be stressed however, that this theory is valid only when dimer-centered basis set is used, while the method described before is valid also in monomer-centered basis sets. In that approach the final expressions for the corrections  $E_{exch}^{(1nm)}$  will involve not only Coulomb integrals, but also exchange and hybrid integrals. When the dimer-centered basis set is used in calculations both approaches are equivalent.

#### 4.1 Hartree-Fock exchange energy $E_{exch}^{(10)}$

The simplest approximation to the first-order exchange energy, neglecting the intramonomer correlation effects, is the Hartree-Fock exchange energy  $E_{exch}^{(100)}$ , defined by Eq. (107) for  $n = m = 0$ . The orbital expression for this correction can be written as

$$\begin{aligned} E_{exch}^{(100)} &= -2[\tilde{v}_{ab}^{ba} + S_{a'}^b(2\tilde{v}_{ab}^{aa'} - \tilde{v}_{ab}^{a'a}) + S_{b'}^a(2\tilde{v}_{ab}^{b'b} - \tilde{v}_{ab}^{bb'}) \\ &\quad - 2S_{a'}^b S_{b'}^a \tilde{v}_{ab}^{ab'} - 2S_{a'}^{b'} S_{b'}^a \tilde{v}_{ab}^{a'b} + S_{a'}^b S_{b'}^a \tilde{v}_{ab}^{a'b'}], \end{aligned} \quad (112)$$

where the generalized two-electron integrals  $\tilde{v}_{ij}^{kl}$  are given by Eq. (67).

## 4.2 First-order intramonomer correlation correction $E_{exch}^{(11)}$

The leading intramonomer correlation correction to  $E_{exch}^{(100)}$  is given by the sum of  $E_{exch}^{(110)}$  and  $E_{exch}^{(101)}$ . Since the appropriate expression for  $E_{exch}^{(101)}$  is obtained from the expression for  $E_{exch}^{(110)}$  by interchanging symbols pertaining to molecules A and B, below we consider only the correction  $E_{exch}^{(110)}$ . Using the fact that  $E_{pol}^{(110)}$  and  $\rho_1^{(1)}(i|j)$  vanish on account of the Brillouin theorem one finds that [34]

$$\begin{aligned} E_{exch}^{(110)} = & -2(2t_{aa'}^{rr'} - t_{a'a}^{rr'})\tilde{v}_{rb}^{aa'}S_{r'}^b - 2(2t_{rr'}^{aa'} - t_{rr'}^{a'a})\tilde{v}_{ab}^{rr'}S_{a'}^b + \\ & + 4\text{Re}(2t_{rr'}^{aa'} - t_{rr'}^{a'a})(\tilde{v}_{a'b}^{r'b'}S_a^bS_{b'}^r - \tilde{v}_{a'b}^{r'b'}S_a^bS_{b'}^r), \end{aligned} \quad (113)$$

where the first-order spin-free cluster amplitude  $t_{rr'}^{aa'}$  is given by Eq. (69). Analogous expression for the correction  $E_{exch}^{(101)}$  can be obtained by the following interchanges:  $a \leftrightarrow b$ ,  $r \leftrightarrow s$ , and  $v(ij) \leftrightarrow v(ji)$ .

## 4.3 Second-order intramonomer correlation correction $E_{exch}^{(12)}$

The intramonomer correlation correction of the second-order is given by the sum  $E_{exch}^{(111)} + E_{exch}^{(120)} + E_{exch}^{(102)}$ . Since the expression for  $E_{exch}^{(102)}$  can be obtained from the expression for  $E_{exch}^{(120)}$  by interchanging symbols pertaining to molecules A and B, it is sufficient to consider only the bilinear term  $E_{exch}^{(111)}$  and the term quadratic in  $W_A$ , i.e.,  $E_{exch}^{(120)}$ .

It can be shown [34] that the bilinear term  $E_{exch}^{(111)}$  is given by

$$\begin{aligned} E_{exch}^{(111)} = & -4\text{Re}(2t_{aa'}^{rr'} - t_{a'a}^{rr'})(2t_{bb'}^{ss'} - t_{b'b}^{ss'})\tilde{v}_{rs}^{ab}S_{r'}^bS_{s'}^{a'} + \\ & -4\text{Re}(2t_{rr'}^{aa'} - t_{rr'}^{a'a})(2t_{bb'}^{ss'} - t_{b'b}^{ss'})\tilde{v}_{as}^{rb}S_{s'}^rS_{a'}^{b'}, \end{aligned} \quad (114)$$

where  $t_{ss'}^{bb'}$  is defined in the same way as  $t_{rr'}^{aa'}$ , i.e.  $t_{ss'}^{bb'} = v_{ss'}^{bb'}/\epsilon_{ss'}^{bb'}$ .

To derive the expression for the correction  $E_{exch}^{(120)}$  it is useful to introduce the following partitioning of  $E_{exch}^{(120)}$

$$E_{exch}^{(120)} = K_2^u(A) + K_2^f(A) + K_{11}^u(A), \quad (115)$$

where  $K_2^f(A)$  and  $K_2^u(A)$  denote the terms linear in  $T_{10}^{(020)}$  and  $T_{20}^{(020)}$ , respectively, and  $K_{11}^u(A)$  is quadratic in  $T_{20}^{(010)}$  [68]. The expression for the component  $K_2^u(A)$  is given by [34]

$$K_2^u(A) = -2(2 \binom{(2)}{t_{aa'}^{rr'}} - \binom{(2)}{t_{a'a}^{rr'}}) \tilde{v}_{rb}^{aa'} S_{r'}^b - 2(2 \binom{(2)}{t_{aa'}^{rr'}} - \binom{(2)}{t_{a'a}^{rr'}}) \tilde{v}_{ab}^{rr'} S_{a'}^b + \\ + 4\text{Re}(2 \binom{(2)}{t_{rr'}^{aa'}} - \binom{(2)}{t_{rr'}^{a'a}}) (\tilde{v}_{a'b}^{r'b'} S_a^b S_{b'}^r - \tilde{v}_{a'b}^{r'b'} S_a^b S_{b'}^r), \quad (116)$$

where the second-order spin-free double excitation cluster amplitude  $\binom{(2)}{t_{aa'}^{rr'}}$  is given by Eq. (78). The orbital formulas for the components  $K_2^f(A)$  and  $K_{11}^u(A)$  can be written as [34]

$$K_2^f(A) = -2[t_a^r \tilde{v}_{rb}^{ba} + t_r^a \tilde{v}_{ab}^{br} + 2t_r^{a'} S_{a'}^b \tilde{v}_{ab}^{ar} + 2t_a^r S_{a'}^b \tilde{v}_{rb}^{aa'} + \\ + 2t_r^a S_{a'}^b \tilde{v}_{ab}^{ra'} + 2t_{a'}^r S_r^b \tilde{v}_{ab}^{aa'} - t_{a'}^r S_r^b \tilde{v}_{ab}^{a'a} - t_r^{a'} S_{a'}^b \tilde{v}_{ab}^{ra} + \\ - t_a^r S_{a'}^b \tilde{v}_{rb}^{a'b} - t_r^a S_{a'}^b \tilde{v}_{ab}^{a'r} + 2t_r^a S_{b'}^r \tilde{v}_{ab}^{b'b} + 2t_a^r S_{b'}^r \tilde{v}_{rb}^{b'b} + \\ - t_r^a S_{b'}^r \tilde{v}_{ab}^{bb'} - t_a^r S_{b'}^r \tilde{v}_{rb}^{bb'} - 4\text{Re} t_r^{a'} S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{ab'} + \\ - 4\text{Re} t_r^a S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{a'b} - 4\text{Re} t_r^{a'} S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{a'b} - 4\text{Re} t_r^a S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{a'b} + \\ + 2\text{Re} t_r^a S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{a'b'} + 2\text{Re} t_r^{a'} S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{a'b'}], \quad (117)$$

$$K_{11}^u(A) = 2(2t_{aa'}^{rr'} - t_{a'a}^{rr'}) t_{r''r'}^{aa'} (2\tilde{v}_{rb}^{br''} + 4S_{a''}^b \tilde{v}_{rb}^{r''a''} - 2S_{a''}^b \tilde{v}_{rb}^{a''r''} + 4S_r^b \tilde{v}_{a''b}^{a''r''} + \\ - 2S_r^b \tilde{v}_{a''b}^{r''a''} + 4S_{b'}^{r''} \tilde{v}_{rb}^{b'b} - 2S_{b'}^{r''} \tilde{v}_{rb}^{bb'} - 4S_{a''}^b S_{b'}^{a''} \tilde{v}_{rb}^{r''b'} - 4S_r^b S_{b'}^{r''} \tilde{v}_{a''b}^{a''b'}) + \\ + 4\text{Re}(2t_{aa'}^{rr'} - t_{a'a}^{rr'}) t_{r''r'}^{aa'} (4S_r^b S_{b'}^{a''} \tilde{v}_{a''b'}^{r''b'} + 2S_r^b S_{b'}^{a''} \tilde{v}_{a''b}^{r''b'}) + \\ - 2(2t_{aa'}^{rr'} - t_{a'a}^{rr'}) t_{rr'}^{a''a'} (2\tilde{v}_{a''b}^{ba} + 4S_{a_1}^b \tilde{v}_{a''b}^{aa_1} - 2S_{a_1}^b \tilde{v}_{a''b}^{a_1a} + 4S_{a''}^b \tilde{v}_{a_1b}^{a_1a} + \\ - 2S_{a''}^b \tilde{v}_{a_1b}^{aa_1} + 4S_{b'}^a \tilde{v}_{a''b}^{b'b} - 2S_{b'}^a \tilde{v}_{a''b}^{bb'} - 4S_{a_1}^b S_{b'}^{a_1} \tilde{v}_{a''b}^{ab'} - 4S_{a''}^b S_{b'}^a \tilde{v}_{a_1b}^{a_1b'}) + \\ - 4\text{Re}(2t_{aa'}^{rr'} - t_{a'a}^{rr'}) t_{rr'}^{a''a'} (4S_{a''}^b S_{b'}^{a_1} \tilde{v}_{a_1b'}^{ab'} + 2S_{a''}^b S_{b'}^{a_1} \tilde{v}_{a_1b}^{ab'}) + \\ - 2(2t_{aa'}^{rr'} - t_{a'a}^{rr'}) t_{r''r_1}^{aa'} (2S_{r'}^b \tilde{v}_{rb}^{r''r_1} + 4S_{r'}^b S_{b'}^{r_1} \tilde{v}_{rb}^{r''b} - 2S_{r'}^b S_{b'}^{r_1} \tilde{v}_{rb}^{r''b'}) + \\ - 2(2t_{aa'}^{rr'} - t_{a'a}^{rr'}) t_{rr'}^{a''a_1} (2S_{a_1}^b \tilde{v}_{a''b}^{aa'} + 4S_{a_1}^b S_{b'}^{a'} \tilde{v}_{a''b}^{ab} - 2S_{a_1}^b S_{b'}^{a'} \tilde{v}_{a''b}^{ab'}) + \\ - 2(2t_{aa''}^{rr''} - t_{a''a}^{rr''}) (2t_{r'r}^{a'a} - t_{r'r}^{a'a}) (S_{a'}^b \tilde{v}_{r''b}^{a''r'} + S_{r''}^b \tilde{v}_{a'b}^{r'a''}) +$$



$$\begin{aligned}
& +4\text{Re}(2t_{aa''}^{rr''} - t_{a''a}^{rr''})(2t_{r'r}^{a'a} - t_{r'r}^{aa'}) (S_{r''}^b S_{b'}^{a''} \tilde{v}_{a'b}^{r'b'} - 2S_{r''}^{b'} S_{b'}^{a''} \tilde{v}_{a'b}^{r'b}) + \\
& 4(2t_{aa''}^{rr''} - t_{a''a}^{rr''})t_{r'r}^{a'a} (-S_{a'}^b \tilde{v}_{r''b}^{r'a''} - S_{r''}^b \tilde{v}_{a'b}^{a''r'} - 2S_{r''}^{b'} S_{b'}^{r'} \tilde{v}_{a'b}^{a''b} + \\
& -2S_{a'}^{b'} S_{b'}^{a''} \tilde{v}_{r''b}^{r'b} + S_{a'}^b S_{b'}^{a''} \tilde{v}_{r''b}^{r'b'} + S_{r''}^b S_{b'}^{r'} \tilde{v}_{a'b}^{a''b'}). \tag{118}
\end{aligned}$$

The spin-free second-order single excitation amplitude  $t_r^a$  is given by Eq. (70). Analogous expressions for the components  $K_2^f(B)$ ,  $K_2^u(B)$ , and  $K_{11}^u(B)$  of the correction  $E_{exch}^{(102)}$  can be obtained by the following interchanges:  $a \leftrightarrow b$ ,  $r \leftrightarrow s$ , and  $v(ij) \leftrightarrow v(ji)$ .

Numerical results through the second-order in  $W_A$  and  $W_B$  obtained thus far [68, 29] show that the convergence of the many-body expansion of the first-order exchange energy is only moderately fast. Therefore, to obtain very accurate results it may be necessary to resort to nonperturbative techniques amounting to a summation of certain classes of diagrams through infinite-order in the correlation operators  $W_A$  and  $W_B$ . The simplest way of performing such infinite-order summations is to approximate the energy  $E_{exch}^{(1)}$  by the expression for the sum  $E_{exch}^{(10)} + E_{exch}^{(12)}$  with first- and second-order cluster amplitudes replaced by the converged amplitudes of the Coupled Cluster Singles and Doubles (CCSD) theory [69]. In this approximation we obtain

$$E_{exch}^{(1)}(CCSD) = E_{exch}^{(100)} + K_2^f(CCSD) + K_2^u(CCSD) + K_{11}^u(CCSD) + K_{11}^{ab}(CCSD), \tag{119}$$

where  $X(CCSD)$  means that the expression  $X$  was computed using the converged cluster amplitudes in the CCSD approximation.  $K_{11}^{ab}(CCSD)$  stands for the expression for the  $E_{exch}^{(111)}$  correction with the first-order cluster amplitudes replaced with the converged CCSD amplitudes, and  $K_2^f(CCSD)$ ,  $K_2^u(CCSD)$ , and  $K_{11}^u(CCSD)$  denote the sum of these components for the monomers A and B, e.g.,  $K_2^f = K_2^f(A) + K_2^f(B)$ .

## 5 Induction energy

The induction energy  $E_{ind}^{(2)}$  represents an important attractive component of the interaction energy. It can be physically interpreted as the interaction of one monomer with the static electric field of the other. For ion-molecule interactions, the induction energy vanishes like  $R^{-4}$  with the intermonomer distance  $R$  and, at least at large distances, it constitutes the dominant contribution to the interaction energy.

When the intramonomer correlation is completely neglected, the induction energy is approximated by the correction of the zeroth order in  $W_A$  and  $W_B$ , i.e. by  $E_{ind}^{(20)}$ . Neglecting the dispersion component of  $E_{pol}^{(20)}$  the induction energy can be written as

$$E_{ind}^{(20)} = E_{ind}^{(20)}(A \leftarrow B) + E_{ind}^{(20)}(B \leftarrow A). \quad (120)$$

The components  $E_{ind}^{(20)}(A \leftarrow B)$  and  $E_{ind}^{(20)}(B \leftarrow A)$  can be interpreted as representing the energy of the induction interaction of the monomer A with the static field of the monomer B, and vice versa, and are defined by

$$E_{ind}^{(20)}(A \leftarrow B) = \langle V S_A \rangle, \quad (121)$$

$$E_{ind}^{(20)}(B \leftarrow A) = \langle V S_B \rangle, \quad (122)$$

where for simplicity the operators  $T_{10}^{(100)}$  and  $T_{01}^{(100)}$  are denoted by  $S_A$  and  $S_B$ , respectively. Using the contraction theorem [42] it is not difficult to show that

$$E_{ind}^{(20)}(A \leftarrow B) = 2 s_r^a (\omega_B)_a^r, \quad (123)$$

where the amplitude  $s_r^a$  is given by

$$s_r^a = (\omega_B)_r^a / \epsilon_r^a. \quad (124)$$

Similar expression for  $E_{ind}^{(20)}(B \leftarrow A)$  can be found by the following interchanges:  $a \leftrightarrow b$ ,  $r \leftrightarrow s$ , and  $B \leftrightarrow A$ . Note, that the problem of calculating the induction energy is very similar to the problem of calculating second-order one-electron properties of molecules [62], and the expression (123) may be viewed as the induction energy

corresponding to the UnCoupled Hartree-Fock (UCHF) scheme. Similarly as in the case of one-electron properties one can define the induction energy corresponding to the Coupled Hartree-Fock (CHF) scheme [62]

$$E_{ind,resp}^{(20)}(A \leftarrow B) = \left( \frac{\partial^2 \mathcal{E}_A^{HF}(\lambda)}{\partial \lambda^2} \right)_{\lambda=0}, \quad (125)$$

where  $\mathcal{E}_A^{HF}(\lambda)$  is the Hartree-Fock approximation to the ground-state energy of the Hamiltonian  $H_A + \lambda \Omega_B$ , where

$$\Omega_B = \sum_{i=1}^{N_A} \omega_B(i).$$

The orbital expression for the CHF induction energy can be written as

$$E_{ind,resp}^{(20)}(A \leftarrow B) = 2 C_r^a (\omega_B)_a^r, \quad (126)$$

where  $C_r^a$  is the CPHF coefficient defined by Eq. (72). Similar expression for  $E_{ind,resp}^{(20)}(B \leftarrow A)$  can be found by the following interchanges:  $a \leftrightarrow b$ ,  $r \leftrightarrow s$ , and  $B \leftrightarrow A$ . Using the perturbation expansion of the CPHF coefficients defined by Eqs. (74)-(75) it is not difficult to prove that the difference  $E_{ind,resp}^{(20)}(A \leftarrow B) - E_{ind}^{(20)}(A \leftarrow B)$  is given by

$$E_{ind,resp}^{(20)}(A \leftarrow B) - E_{ind}^{(20)}(A \leftarrow B) = 2 \sum_{n=1}^{\infty} (\omega_B)_a^r C_r^{(n)a}. \quad (127)$$

Equation (127) clearly shows that the correction  $E_{ind,resp}^{(20)}$  sums up to infinity certain diagrams appearing in the many-body expansion of the induction energy based on Eq. (24). Specifically, one can prove that the CHF induction energy can be represented by the sum of “linear” diagrams without rings. Therefore, the induction energy in the CHF scheme fully accounts for the so-called apparent correlation or selfconsistency effects [62] and is included in the supermolecular Hartree-Fock interaction energy. Fortunately, the numerical experience in calculating polarizabilities [70, 71, 72] suggests that the true correlation contributions are much smaller than the apparent one. Thus, the approximation of the total induction energy by the correction  $E_{ind,resp}^{(20)}$  seems to be reasonable.

Sometimes the dispersion corrections  $E_{disp}^{(20)}$  or  $E_{disp}^{(21)}$  are also referred to as “apparent” correlation effects [73]. This terminology is a rather unfortunate extension of that used for the induction energy.  $E_{disp}^{(200)}$ ,  $E_{disp}^{(210)}$ , and all the other dispersion energy corrections represent the *true* correlation since, by the very definition of the dispersion energy, their diagrammatic representation contains at least one ring [74], and no dispersion energy component is included in the HF interaction energy [62, 75].

## 6 Exchange-induction energy

The exchange-induction energy can be physically interpreted as representing the coupling of the electron exchange with the induction interaction. In this section we report the expression for the leading term of the many-body expansion of the exchange-induction energy  $E_{exch-ind}^{(20)}$ . In deriving this expression the single-exchange approximation has been assumed. Higher-order terms (in  $S^2$ ) have been computed for the helium dimer and found to be negligible in the region of the van der Waals minimum [76]. With this approximation the leading, single-exchange term in the exchange-induction energy can be written as

$$E_{exch-ind}^{(20)} = E_{exch-ind}^{(20)}(A \leftarrow B) + E_{exch-ind}^{(20)}(B \leftarrow A), \quad (128)$$

where for example  $E_{exch-ind}^{(20)}(A \leftarrow B)$  can be physically interpreted as the coupling the electron exchange with the induction interaction of the monomer A with the static field of the monomer B. The components  $E_{exch-ind}^{(20)}(A \leftarrow B)$  and  $E_{exch-ind}^{(20)}(B \leftarrow A)$  are given by

$$E_{exch-ind}^{(20)}(A \leftarrow B) = \langle (V - \langle V \rangle)(P_1 - \langle P_1 \rangle)S_A \rangle, \quad (129)$$

$$E_{exch-ind}^{(20)}(B \leftarrow A) = \langle (V - \langle V \rangle)(P_1 - \langle P_1 \rangle)S_B \rangle. \quad (130)$$

The expression for the second-order exchange-induction energy has been derived in Ref. [36] and written in the form of a many-orbital cluster expansion. In terms of

one- and two-electron orbital integrals this correction can be expressed as

$$\begin{aligned}
E_{exch-ind}^{(20)}(A \leftarrow B) = & -2[s_r^a \tilde{v}_{ab}^{br} + 2s_r^{a'} S_{a'}^b \tilde{v}_{ab}^{ar} + 2s_r^a S_{a'}^b \tilde{v}_{ab}^{ra'} - s_r^{a'} S_{a'}^b \tilde{v}_{ab}^{ra} + \\
& -s_r^a S_{a'}^b \tilde{v}_{ab}^{a'r} + 2s_r^a S_{b'}^r \tilde{v}_{ab}^{b'b} - s_r^a S_{b'}^r \tilde{v}_{ab}^{bb'} - 2s_r^{a'} S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{ab'} + \\
& -2s_r^a S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{rb'} - 2s_r^a S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{a'b} - 2s_r^{a'} S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{rb} + \\
& + s_r^a S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{a'b'} + s_r^{a'} S_{a'}^b S_{b'}^r \tilde{v}_{ab}^{rb'}], \tag{131}
\end{aligned}$$

where  $s_r^a$  is defined by Eq. (124). Analogous expression for  $E_{exch-ind}^{(20)}(B \leftarrow A)$  can be obtained by the following interchanges:  $a \leftrightarrow b$ ,  $r \leftrightarrow s$ , and  $v(ij) \leftrightarrow v(ji)$ .

Similarly, as in the case of the induction energy, one can introduce the CHF exchange-induction energy  $E_{exch-ind,resp}^{(20)}$  [77]. The orbital expression for this correction can be easily found by substituting in Eq. (131) the CPHF coefficients  $C_r^a$  for the amplitudes  $s_r^a$ .

## 7 Dispersion energy

Among various SAPT corrections, the dispersion energy plays a special role. For the interaction of neutral molecules, the dispersion energy represent the main attractive component of the interaction energy. The long-range dispersion interactions are of great importance for a variety of physical properties, such as the equilibrium structure of molecular and rare-gas crystals, the transport properties of gases and liquids, and scattering cross-sections. The expansion of the dispersion energy in terms of the intramonomer correlation operators  $W_A$  and  $W_B$  can be obtained as described in Sec. 2. The only new aspect is that the corrections of the second order in  $V$ ,  $E_{pol}^{(2ij)}$ , contain two physically distinct contributions: the dispersion component,  $E_{disp}^{(2ij)}$ , and the induction component,  $E_{ind}^{(2ij)}$ . The separation of these two components can be most easily performed by invoking the diagrammatic representation of the perturbation theory corrections. An induction energy diagram must be disconnected on one side of the intermolecular “border” (like the static polarizability diagrams) since it has to contain two times the representation of the electrostatic potential of

the monomer. In contrast, the dispersion energy diagrams are connected on both sides of this “border” (like the correlation energy diagrams). In this Section we will present formulas for the dispersion energy corrections  $E_{disp}^{(2l)}$  through second order in  $W$ , i.e., for  $l \leq 2$ .

## 7.1 Hartree-Fock dispersion energy $E_{disp}^{(20)}$

When the intramonomer correlation is completely neglected, the dispersion energy is approximated by the correction of the zeroth order in  $W_A$  and  $W_B$ , i.e. by  $E_{disp}^{(20)}$ . This correction represents the dispersion interaction of molecules described at the Hartree-Fock level of approximation and therefore may be referred to as the *Hartree-Fock dispersion energy*. Neglecting the induction component of  $E_{pol}^{(20)}$  we obtain the following expression for the dispersion part

$$E_{disp}^{(20)} = \langle VS \rangle, \quad (132)$$

where for simplicity the operator  $T_{11}^{(100)}$  is denoted by  $S$ .

Using the spin-free forms of  $V$  and  $S$  [32], one finds that

$$E_{disp}^{(20)} = 4 v_{rs}^{ab} v_{ab}^{rs} / \epsilon_{rs}^{ab}. \quad (133)$$

The above expression has a particularly simple form, so that the “Hartree-Fock” dispersion energy can easily be calculated for large polyatomic molecules. It is worthwhile to add that  $E_{disp}^{(20)}$  can also be calculated variationally using arbitrary basis [78, 27] by minimizing the functional  $J[\tilde{T}_{11}] = \langle \tilde{T}_{11} | [F_A + F_B, \tilde{T}_{11}] \rangle + 2\text{Re} \langle \tilde{T}_{11} | V \rangle$ , where  $\tilde{T}_{11}$  is a trial operator of the form of Eq. (22).

## 7.2 First-order intramonomer correlation correction $E_{disp}^{(21)}$

The leading intramonomer correlation correction to  $E_{disp}^{(20)}$  is of the first order in  $W$  and is given by  $E_{disp}^{(21)}$ , i.e. by the sum of  $E_{disp}^{(210)}$  and  $E_{disp}^{(201)}$ . Since the appropriate expression for  $E_{disp}^{(201)}$  is obtained from the expression for  $E_{disp}^{(210)}$  by interchanging symbols pertaining to molecules A and B, below we consider only the correction  $E_{disp}^{(210)}$ .

Neglecting components contributing only to the induction energy, we obtain the dispersion part of  $E_{pol}^{(210)}$

$$E_{disp}^{(210)} = \langle S | [W_A, S] \rangle + 2\text{Re} \langle T_A | [V, S] \rangle, \quad (134)$$

where  $T_A$  denotes the cluster operator  $T_{20}^{(010)}$ .

The expansion of  $E_{disp}^{(210)}$  in terms of molecular integrals can be performed using the technique described in Ref. [32]. The result of this expansion is

$$E_{disp}^{(210)} = 2 t_{rs}^{ab} g_{ar'}^{ra'} t_{a'b}^{r's} + 4 \text{Re} t_{rs}^{ab} v_{r'b}^{a's} \theta_{aa'}^{rr'}, \quad (135)$$

where  $\theta_{aa'}^{rr'} \equiv 4t_{aa'}^{rr'} - 2t_{a'a}^{rr'} = (\theta_{rr'}^{aa'})^*$ ,

$$t_{rs}^{ab} \equiv v_{rs}^{ab} / \epsilon_{rs}^{ab}, \quad t_{ab}^{rs} \equiv (t_{rs}^{ab})^* \quad (136)$$

and

$$g_{ll'}^{kk'} = 4v_{ll'}^{kk'} - 2v_{l'l}^{kk'}, \quad (137)$$

for arbitrary indices  $k, k', l, l'$  (corresponding to either occupied or unoccupied orbitals from both molecules).

### 7.3 Second-order intramonomer correlation correction $E_{disp}^{(22)}$

The intramonomer correlation correction of the second order in  $W = W_A + W_B$  is given by  $E_{disp}^{(22)} = E_{disp}^{(211)} + E_{disp}^{(220)} + E_{disp}^{(202)}$ . Since the expression for  $E_{disp}^{(202)}$  can be obtained from the expression for  $E_{disp}^{(220)}$  by interchanging symbols pertaining to molecules A and B, it is sufficient to consider only the bilinear term  $E_{disp}^{(211)}$  and the term quadratic in  $W_A$ , i.e.  $E_{disp}^{(220)}$ .

#### 7.3.1 Bilinear term $E_{disp}^{(211)}$

Since the first-order in  $W_A$  ( $W_B$ ) intramonomer correlation correction to the electrostatic potential  $\Omega_A$  ( $\Omega_B$ ) vanishes due to the Brillouin theorem, there is no bilinear contribution to the induction energy, i.e.  $E_{ind}^{(211)} = 0$ . Thus,  $E_{pol}^{(211)}$  contains

only a purely dispersion contribution:  $E_{pol}^{(211)} = E_{disp}^{(211)}$ . Employing Eq. (24) and verifying that the term quadratic in  $T$  does not contribute we can write

$$E_{disp}^{(211)} = 2\text{Re} < [V, T_A] + [W_A, S] | \Re_{11}([V, T_B] + [W_B, S]) > + 2\text{Re} < S | [[V, T_A], T_B] >, \quad (138)$$

where  $T_B$  denotes the operator  $T_{02}^{(010)}$ . The expansion of this expression into two-electron integrals gives

$$E_{disp}^{(211)} = 2\text{Re} P_{rs}^{ab} Q_{ab}^{rs} / \epsilon_{rs}^{ab} + 2\text{Re} \theta_{rr'}^{aa'} \theta_{ss'}^{bb'} v_{a'b}^{r's} t_{ab'}^{r's'} \quad (139)$$

where  $P_{rs}^{ab}$  and  $Q_{ab}^{rs} = (Q_{ab}^{rs})^*$  are proportional to the amplitudes mentioned above

$$P_{rs}^{ab} = \theta_{ss'}^{bb'} v_{rb'}^{as'} + t_{rs'}^{ab'} g_{b's}^{s'b} \quad (140)$$

$$Q_{rs}^{ab} = \theta_{rr'}^{aa'} v_{sa'}^{br'} + t_{r's}^{a'b} g_{a'r}^{r'a} \quad (141)$$

The quantities  $\theta_{ss'}^{bb'}$  are defined in the same way as  $\theta_{rr'}^{aa'}$ , i.e.  $\theta_{bb'}^{ss'} = 4t_{ss'}^{bb'} - 2t_{ss'}^{b'b}$ ,  $t_{ss'}^{bb'} = v_{ss'}^{bb'} / \epsilon_{ss'}^{bb'}$  while  $g_{b's}^{s'b}$  and  $g_{a'r}^{r'a}$  are defined according to Eq. (137).

### 7.3.2 Quadratic term $E_{disp}^{(220)}$

In contrast to  $E_{pol}^{(211)}$  the correction  $E_{pol}^{(220)}$  contains both induction and dispersion contributions, which have to be separated out. The resulting expression for  $E_{disp}^{(220)}$  separates naturally into contributions, which, using the terminology commonly accepted in the many-body theory, originate from single, double, triple, and quadruple excitations:

$$E_{disp}^{(220)} = E_{disp}^{(220)}(S) + E_{disp}^{(220)}(D) + E_{disp}^{(220)}(T) + E_{disp}^{(220)}(Q). \quad (142)$$

The specific formulas for these contributions are:

$$E_{disp}^{(220)}(S) = 2\text{Re} < [V, S] | \Re_{10}([W_A, T_A]) > \quad (143)$$

$$E_{disp}^{(220)}(D) = 2\text{Re} < [V, S] | \Re_{20}([W_A, T_A]) > + < [V, T_A] + [W_A, S] | \Re_{11}([V, T_A] + [W_A, S]) > \quad (144)$$



$$E_{disp}^{(220)}(T) = < [V, T_A] + [W_A, S] | \Re_{21}([V, T_A] + [W_A, S]) > \quad (145)$$

$$E_{disp}^{(220)}(Q) = < T_A | [[V, T_A], S] > + < S | [[W_A, T_A], S] > \quad (146)$$

It is worthwhile to note that the second term in Eq. (144) and the whole contribution from triple excitations are always negative since the resolvents  $\Re_{11}$  and  $\Re_{21}$  are negative definite.

The corresponding final formula for  $E_{disp}^{(220)}(S)$  can be written as

$$E_{disp}^{(220)}(S) = 4\text{Re}X_r^a Y_a^r / \epsilon_a^r \quad (147)$$

where

$$X_r^a = g_{a'r}^{r'r'} t_{r'r'}^{a'a'} - g_{a'a''}^{a'r'} t_{r'r'}^{a'a''} \quad (148)$$

and

$$Y_a^r = v_{r's}^{r'b} t_{ab}^{r's} - v_{as}^{a'b} t_{a'b}^{rs}, \quad (149)$$

All symbols used above were defined previously in Eqs. (69), (136), and (137).

The formula for  $E_{disp}^{(220)}(D)$  is

$$E_{disp}^{(220)}(D) = 2\text{Re}(2Z_{rr'}^{aa'} - Z_{rr'}^{aa'}) U_{aa'}^{rrr'} / \epsilon_{rr'}^{aa'} + D_{ab}^{rs} D_{rs}^{ab} / \epsilon_{rs}^{ab}, \quad (150)$$

where the intermediate quantities  $D_{ab}^{rs}$ ,  $Z_{rr'}^{aa'}$  and  $U_{aa'}^{rrr'}$  are defined as follows

$$D_{rs}^{ab} = v_{a's}^{r'b} \theta_{rr'}^{aa'} + g_{ra'}^{ar'} t_{r's}^{a'b}, \quad (151)$$

$$Z_{rr'}^{aa'} = v_{rb}^{as} t_{r's}^{a'b} + v_{r'b}^{a's} t_{rs}^{ab} \quad (152)$$

and

$$\begin{aligned} U_{aa'}^{rrr'} &= v_{r'r'''}^{r'r'} t_{a'a'}^{r''r'''} + v_{a''a'''}^{a''a'} t_{a''a'''}^{r'r'} + \frac{1}{2} v_{a'r''}^{r'a''} \theta_{aa''}^{rr''} + \frac{1}{2} v_{ar''}^{ra''} \theta_{a'a''}^{r'r''} \\ &- v_{a'r''}^{a''r'} t_{aa''}^{r'r''} - v_{ar''}^{a''r} t_{a'a''}^{r'r''} - v_{a'r''}^{a''r'} t_{a'a''}^{r'r''} - v_{a'r''}^{a''r} t_{a'a''}^{r'r''}. \end{aligned} \quad (153)$$

The formula for  $E_{disp}^{(220)}(T)$  is

$$E_{disp}^{(220)}(T) = (4W_{rr's}^{aa'b} - 2W_{rr's}^{a'ab}) W_{aa'b}^{rrr's} / \epsilon_{rr's}^{aa'b}, \quad (154)$$

where

$$\begin{aligned}
W_{rr's}^{aa'b} &= v_{r's}^{r''b} t_{rr''}^{a a'} + v_{r s}^{r''b} t_{r''r'}^{a a'} - v_{a''s}^{a'b} t_{rr'}^{a a''} - v_{a''s}^{a b} t_{r r'}^{a'' a'} \\
&+ v_{r r'}^{r'' a'} t_{r''s}^{a b} + v_{r r'}^{a r''} t_{r''s}^{a' b} - v_{a''r'}^{a a'} t_{r s}^{a'' b} - v_{a''r'}^{a a'} t_{r' s}^{a'' b} .
\end{aligned} \tag{155}$$

and  $W_{aa'b}^{rr's} = (W_{rr's}^{aa'b})^*$ . It is obvious that the evaluation of the three-particle correlation contribution to the dispersion energy, given by Eqs. (154) and (155), is the most time consuming part of the evaluation of  $E_{disp}^{(220)}$ .

The quadruple excitation contribution to  $E_{disp}^{(220)}$  is represented by

$$\begin{aligned}
E_{disp}^{(220)}(Q) &= v_{a''b}^{r''s} \theta_{aa'}^{rr'} \theta_{r'r''}^{a'a''} t_{rs}^{ab} - 2t_{rr''}^{aa'} \theta_{aa'}^{rr'} v_{r's}^{a''b} t_{a''b}^{r''s} - 2t_{rr'}^{aa''} \theta_{aa'}^{rr'} v_{r''s}^{a'b} t_{a''b}^{r''s} \\
&+ t_{a''b}^{r''s} g_{aa'}^{rr'} \theta_{r'r''}^{a'a''} t_{rs}^{ab} - 2t_{aa'}^{rr''} g_{rr'}^{aa'} t_{r''s}^{a''b} t_{a''b}^{r''s} - 2t_{aa'}^{rr'} g_{rr'}^{aa'} t_{r''s}^{a''b} t_{a''b}^{r''s} .
\end{aligned} \tag{156}$$

It is worthwhile to remark that second term of the double excitation part (144) and the triple excitation part (145) of the correction  $E_{disp}^{(220)}$  can also be calculated variationally using arbitrary basis [32] by minimizing the functionals

$$J[\tilde{T}_{11}] = \langle \tilde{T}_{11} | [F_A + F_B, \tilde{T}_{11}] \rangle + 2\text{Re} \langle \tilde{T}_{11} | [V, T_A] + [W_A, S] \rangle . \tag{157}$$

$$J[\tilde{T}_{21}] = \langle \tilde{T}_{21} | [F_A + F_B, \tilde{T}_{21}] \rangle + 2\text{Re} \langle \tilde{T}_{21} | [V, T_A] + [W_A, S] \rangle , \tag{158}$$

where  $\tilde{T}_{11}$  and  $\tilde{T}_{21}$  are trial operators of the form of Eq. (22).

## 8 Exchange-dispersion energy

The exchange-dispersion energy can be physically interpreted as representing the coupling of the electron exchange with the dispersion interaction. In this section we report the expression for the leading term of the many-body expansion of the exchange-dispersion energy  $E_{exch-disp}^{(20)}$ . In deriving this expression the single-exchange approximation has been assumed. Higher-order terms (in  $S^2$ ) have been computed for the  $\text{He}_2$  system and found to be negligible in the region of the van der Waals minimum [76]. With this approximation the leading, single-exchange term in

the exchange-dispersion energy can be written as

$$E_{exch-disp}^{(20)} = \langle (V - \langle V \rangle) (P_1 - \langle P_1 \rangle) S \rangle. \quad (159)$$

The expression for the second-order exchange-dispersion energy has been derived in Ref. [36] in terms of geminals. In terms of one- and two-electron orbital integrals this correction can be expressed as

$$E_{exch-disp}^{(20)} = -2(\tilde{v}_{ab}^{sr} + h_{ab}^{rs} + q_{ab}^{rs})t_{rs}^{ab} \quad (160)$$

where the quantities  $h_{ab}^{rs}$  and  $q_{ab}^{rs}$  contain the hybrid and the Coulomb integrals, respectively, and are defined by

$$\begin{aligned} h_{ab}^{rs} = & S_a^s(2\tilde{v}_{a'b}^{a'r} - \tilde{v}_{a'b}^{ra'}) + S_{a'}^s(2\tilde{v}_{ab}^{ra'} - \tilde{v}_{ab}^{a'r}) \\ & + S_b^r(2\tilde{v}_{ab'}^{sb'} - \tilde{v}_{ab'}^{b's}) + S_{b'}^r(2\tilde{v}_{ab}^{b's} - \tilde{v}_{ab}^{sb'}), \end{aligned} \quad (161)$$

$$\begin{aligned} q_{ab}^{rs} = & S_b^r S_{a'}^{b'} \tilde{v}_{ab'}^{a's} - 2S_{b'}^r S_{a'}^{b'} \tilde{v}_{a'b}^{a's} - 2S_b^r S_a^{b'} \tilde{v}_{a'b'}^{a's} + 4S_{b'}^r S_a^{b'} \tilde{v}_{a'b}^{a's} \\ & + S_a^s S_b^{a'} \tilde{v}_{a'b'}^{rb'} - 2S_{a'}^s S_b^{a'} \tilde{v}_{ab'}^{rb'} - 2S_a^s S_{b'}^{a'} \tilde{v}_{a'b}^{rb'} + 4S_{a'}^s S_{b'}^{a'} \tilde{v}_{ab}^{rb'} \\ & + S_{b'}^r S_{a'}^s \tilde{v}_{ab}^{a'b'} - 2S_b^r S_{a'}^s \tilde{v}_{ab'}^{a'b'} - 2S_{b'}^r S_a^s \tilde{v}_{a'b}^{a'b'} \\ & + S_b^{a'} S_a^{b'} \tilde{v}_{a'b'}^{rs} - 2S_b^{a'} S_{a'}^{b'} \tilde{v}_{ab'}^{rs} - 2S_{b'}^{a'} S_a^{b'} \tilde{v}_{a'b}^{rs}. \end{aligned} \quad (162)$$

## 9 Applications

The theory developed in the previous sections has been applied to several interacting atoms and molecules. Table 2 presents several representative calculations for near van der Waals minimum geometries. For the systems which were investigated some time ago not all the corrections are available. We have listed in Table 2 both the standard and response versions of the corrections (when available) for comparison, however, in actual calculations only one variant needs to be computed. Table 2 allows to draw conclusions about the importance of various corrections for different systems. The relative magnitudes of the particular corrections can be connected with the properties of interacting monomers. For a detailed discussion of this problem we refer to the original papers.

It can be shown [75] that the Hartree-Fock interaction energy  $E_{int}^{HF}$ , defined as the difference of the Hartree-Fock energies for the complex and for the free monomers, is a sum of certain SAPT corrections. Specifically, the corrections  $E_{pol}^{(10)}$ ,  $E_{exch}^{(10)}$ ,  $E_{ind}^{(20)}$ , and some higher order induction and exchange corrections are included in  $E_{int}^{HF}$ . Thus,  $E_{int}^{HF}$  can be represented as

$$E_{int}^{HF} = E_{pol}^{(10)} + E_{exch}^{(10)} + E_{ind,resp}^{(20)} + E_{exch-ind,resp}^{(20)} + \delta E_{int}^{HF}, \quad (163)$$

where  $\delta E_{int}^{HF}$  collects all higher-order induction and exchange corrections. Equation (163) allows one to incorporate the Hartree-Fock interaction energy  $E_{int}^{HF}$  into the expression for the SAPT intermolecular potential. In this way we effectively sum various high-order induction and exchange corrections included in  $E_{int}^{HF}$ . Since with the rather large basis sets used by us the SCF interaction energy is already very well converged, this approach does not bring with it all the usual basis set superposition error problems connected with the supermolecular approach.

The results presented in Table 2 allow us to draw conclusions about the performance of the many-body SAPT. For three out of six systems presented in Table 2 the empirical interactions are known to a very high accuracy, probably of the order of one percent. These systems are  $\text{He}_2$ ,  $\text{Ar-H}_2$ , and  $\text{Ar-HF}$ . Actually, the  $\text{Ar-H}_2$  empirical potential is considered to be the most accurate of any interacting systems. For these systems our SAPT result is very close to the empirical interaction energy. For  $\text{Ar-H}_2$  and  $\text{Ar-HF}$  these results represent the first *ab initio* calculations which achieved such a high agreement with experiments. There are two factors which contribute to this agreement. First, for those systems virtually all the corrections developed by us have been computed. Second, rather large basis sets containing in some cases even the  $h$ -symmetry orbitals have been used. We may conclude that our approach takes now into account all the important components of the interaction energy. We have observed that some corrections are relatively slowly convergent with the size of the basis set and the inclusion of the  $g$ -symmetry functions is required to achieve accuracies better than about 10 percent.

The agreement between the SAPT results and the empirical interaction energies

is very good also for the water dimer and the uracil–water systems. Since in those cases only a subset of corrections have been computed and the basis sets were not as large as for the previously discussed systems, this agreement has to be to some extent fortuitous. At the same time the empirical depths of the potentials are known to a much lesser accuracy. Actually, in Ref. [32] we estimate that the exact depth of the minimum for the water dimer should be about 0.5 – 1 kcal/mole smaller than our computed value, indicating that also the empirical estimate is too large.

He–F<sup>−</sup> is an example of a system for which our calculations suggest a revision of the accepted potential energy curve. The empirical result differs significantly from the value computed using SAPT. The empirical potentials for rare gas atoms interacting with halide ions were considered to be quite accurate since these potentials have been obtained rather directly from experimental data and agreed very well with the semiempirical potentials [99]. It should be stressed, that although the empirical potential was obtained by a direct inversion of the ion mobility data [100], it is available only for small  $R$  and has been extrapolated to the minimum distance by using input from semiempirical calculations [89]. The validity of this potential was questioned before by Sadlej and Dierksen [95] on the basis of supermolecular MBPT4 calculations in large, interaction optimized basis sets. The MBPT4 theory, however, exhibits a rather erratic convergence pattern in this case, raising questions about possible importance of higher-order corrections. Our SAPT calculation agrees well with the supermolecular MBPT4 result and the convergence pattern of the latter theory can be rationalized by relating the two approaches.

## 10 Discussion and conclusions

We have developed a computer program for calculations of the intermolecular interaction energies for closed-shell systems. The major features of this approach are as follows:

- (i) The intermolecular interaction energy, unlike in the traditional supermolecular method, is calculated directly as a sum of well defined physical contributions.

This reveals the physical nature of the intermolecular interaction and the connection between its strength and the properties (both static and dynamic) of the interacting molecules.

- (ii) Since the interaction energy is obtained directly (not as a difference of large numbers), it is free from the basis set superposition error plaguing the supermolecular calculations.
- (iii) All components of the interaction energy are size-extensive, which enables applications to spatially extended polyatomic molecules.
- (iv) Different energy corrections exhibit different radial and angular dependence, which can be examined in great detail from the point of view of achieving state-of-the-art analytical fits in terms of physically interpretable parameters.
- (v) Since the individual energy corrections show very different basis set requirements, it is advantageous to calculate them separately with specifically optimized basis sets.
- (vi) Although our expressions are similar to those of the supermolecular MBPT, the overall computational effort is smaller than in the standard MBPT calculation of equivalent order since the orbital summation ranges are shorter. This feature follows from the fact that the most time consuming components of SAPT can be computed in the monomer-centered basis set while the supermolecular approach always requires at least one calculation in the full dimer basis. This enables SAPT applications with larger basis sets and to larger molecules than it was previously possible at the correlated *ab initio* level. The largest application so far was to the interaction of uracil molecule with water and we estimate that calculations for systems with over 100 electrons are feasible at present.
- (vii) Since our interaction energy components are implicitly included in the supermolecular MBPT interaction energy of appropriate order, the knowledge of

their angular and radial dependence and of basis set requirements is essential for an optimal design and error estimation in the supermolecular calculations.

The numerical results obtained for the systems discussed in the preceding section allow us to examine the performance of SAPT. We see that the majority of the SAPT corrections converge relatively fast with the size of basis set. The corrections which converge somewhat slower happen to be those which are the easiest to compute, therefore large basis sets can be used to obtain their saturated values. Our computed SAPT or SCF+SAPT interaction energies at the minimum configurations are very close to the experimental values for all the systems considered, except for  $\text{He-F}^-$ . The SAPT system of codes enables routine calculations of intermolecular interaction potentials for medium size molecules. The results appear to be more reliable than those obtained by the supermolecular MBPT approach.

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## 11 Captions to Table 2

<sup>a</sup> $R = 5.6$  bohr.

<sup>b</sup> $R = 6.5$  bohr.

<sup>c</sup>Linear geometry,  $R = 6.7$  bohr.

<sup>d</sup>Linear Ar–HF geometry. The distance between Ar and the center of mass of HF is 7.27976 bohr.

<sup>e</sup>Geometry as defined in Table III of Ref. [32] except that the O–O distance is 2.95 Å and the angle between the O–O axis and the HOH bisector of the proton acceptor is 120°.

<sup>f</sup>Geometry optimized in Ref. [86] specified in Fig. 1 of Ref. [85].

<sup>g</sup> $\delta E_{int}^{HF} = E_{int}^{HF} - E_{pol}^{(10)} - E_{exch}^{(10)} - E_{ind,resp}^{(20)}$ . If computed, the correction  $E_{exch-ind,resp}^{(20)}$  is also subtracted. For those cases where the corrections with response are not available, the corrections  $E_{ind}^{(20)} + E_{exch-ind}^{(20)}$  are used.

<sup>h</sup> $E_{int}^{HF}$  is computed with the CP correction.

<sup>i</sup> $\varepsilon_{exch}^{(1)}(\text{CCSD}) = E_{exch}^{(1)}(\text{CCSD}) - E_{exch}^{(10)}$ .

<sup>j</sup>Results obtained using a Gaussian type geminal (GTG) basis set. The values of the consecutive corrections in the  $[7s4p2d1f]$  basis are -0.03243, -0.00601, and 0.0081, respectively.

<sup>k</sup>This correction was computed in a  $[7s4p3d2f2g1h/3s3p2d1f]$  basis.

<sup>l</sup>The triple excitation part not included.

<sup>m</sup>Computed in two-orbital approximation [87].

<sup>n</sup> $E_{int} = E_{int}^{HF} + \text{SAPT}_{corr}$  where  $\text{SAPT}_{corr}$  is the sum of the preceding corrections listed below the  $E_{int}^{HF}$  line. The response and CCSD versions of the corrections are taken when available.

<sup>o</sup>In computing the total energy for He<sub>2</sub> the correction  $\varepsilon_{exch}^{(1)}(\text{GTG}) = 0.00208$  from Ref. [28] was used instead of  $\varepsilon_{exch}^{(1)}(\text{CCSD})$ .

<sup>p</sup>Aziz *et al.*, Ref. [88]

<sup>q</sup>Koutselos, Mason, and Viehland, Ref. [89].

<sup>r</sup>Le Roy and Hutson, Ref. [90]

Table 1: List of the corrections included in the SAPT system of programs. The perturbation theory is based on the partitioning of the total Hamiltonian as  $H = F + V + W$ , where the zeroth-order operator  $F = F_A + F_B$  is the sum of the Fock operators for the monomers, the intermolecular potential  $V = H - H_A - H_B$  is the difference between the Hamiltonians of interacting and noninteracting systems, and the fluctuation potential  $W = W_A + W_B$  is the sum of the Moller-Plesset fluctuation potentials of the monomers:  $W_C = H_C - F_C$ . All corrections include the damping due to the charge overlap effects. The superscripts  $n$  and  $l$  in a correction  $E^{(nl)}$  denote the orders of perturbation in  $V$  and in  $W$ , respectively.

Symbol	Equation	Name	Physical Interpretation
$E_{pol}^{(10)}$	(66)	Electrostatic energy	Accounts for damped electrostatic interactions of uncorrelated (computed at the Hartree-Fock approximation) permanent electric multipole moments of the monomers.
$E_{pol}^{(1l)}$ $l = 2 - 4$	(68), (76), (77), (84), (87)	Intramonomer correlation correction to electrostatic energy	Account for damped electrostatic interaction of correlated multipole moments of the monomers. Contain correlation effects of the $l$ th-order in $W$ .
$E_{exch}^{(10)}$	(112)	Exchange repulsion	Results from exchange of electrons (quantum mechanical tunneling) between unperturbed monomers described at the Hartree-Fock level.
$E_{exch}^{(1l)}$ $l = 1, 2$	(113), (114), (115)	Intramonomer correlation correction to exchange repulsion	Account for the effects of the intramonomer correlation (of the $l$ th order in $W$ ) on the exchange repulsion.
$E_{ind}^{(20)}$	(123), (126)	Induction energy	Originates from the damped interactions between the permanent and induced multipole moments obtained in the Hartree-Fock approximation.
$E_{exch-ind}^{(20)}$	(131)	Exchange-induction energy	Additional exchange repulsion due to the coupling of electron exchange and the induction interaction in zeroth order with respect to $W$ .
$E_{disp}^{(20)}$	(133)	Dispersion energy	Originates from damped interactions of <i>instantaneous</i> electric multipole moments of the monomers described at the Hartree-Fock approximation.
$E_{exch-disp}^{(20)}$	(160)	Exchange-dispersion energy	Additional exchange repulsion due to the coupling of electron exchange and the dispersion interaction in zeroth order with respect to $W$ .
$E_{disp}^{(2l)}$ $l = 1, 2$	(135), (139), (147), (150), (154), (156)	Intramonomer correlation correction to dispersion energy	Intramonomer correlation correction (of the $l$ th order in $W$ ) to the dispersion energy. Originates from the coupling of the intramonomer correlation effects and the intermolecular dispersion interaction.



Table 2: Many-body SAPT energies for several representative interacting systems at geometries close to van der Waals minima. All energies are in kcal/mol. All calculations were performed in dimer-centered basis sets.

System:	He <sub>2</sub> <sup>a</sup>	HeF <sup>-b</sup>	Ar-H <sub>2</sub> <sup>c</sup>	Ar-HF <sup>d</sup>	(H <sub>2</sub> O) <sub>2</sub> <sup>e</sup>	Uracil-water <sup>f</sup>
Reference:	[68] and present	[29]	[30]	[84]	[32]	[85]
Basis:	[7s4p2d1f]	[5s3p2d/ 5s3p2d]	[7s4p3d2f1g/ 3s2p1d]	[7s4p3d2f1g/ 5s3p2d1f/ 3s2p1d]	[5s3p2d1f/ 3s2p1d]	[2s1p1d/ 1s1p]
$E_{pol}^{(10)}$	-0.00310	-0.0287	-0.0765	-0.0348	-7.79	-15.15
$E_{exch}^{(10)}$	0.02235	0.1322	0.3012	0.1904	6.16	9.89
$E_{ind}^{(20)}$	-0.00046		-0.0686	-0.2217	-2.13	-4.50
$E_{ind,resp}^{(20)}$	-0.00050	-0.2506	-0.0782	-0.2526		
$E_{exch-ind}^{(20)}$	0.00036		0.0596	0.0374		
$E_{exch-ind,resp}^{(20)}$	0.00041		0.0684	0.0450		
$\delta E_{int}^{HFg}$	-0.00084	0.0001	-0.0200	-0.0289	0.19	0.43
$E_{int}^{HFh}$	0.01832	-0.1470	0.1949	-0.0809	-3.57	-9.33
$E_{pol}^{(12)}$	-0.00019		-0.0049	-0.0194	0.21	1.55
$E_{pol,resp}^{(12)}$	-0.00026	-0.0294	-0.0061	-0.0184		
$E_{pol}^{(13)}$	-0.00011		0.0004	0.0082		
$E_{pol,resp}^{(13)}$	-0.00007	0.0192	0.0010	0.0058		
$E_{pol,resp}^{(14)}$	-0.00003	-0.0365				
$E_{exch}^{(11)}$	0.00043	0.0014	0.0148	0.0080		
$E_{exch}^{(12)}$	0.00091	0.1155	0.0097	0.0394		
$\varepsilon_{exch}^{(1)}(\text{CCSD})^i$	0.00255	0.1527				
$E_{disp}^{(20)}$	-0.03422 <sup>j</sup>	-0.0770	-0.3698 <sup>k</sup>	-0.3372	-2.07	-3.12
$E_{disp}^{(21)}$	-0.00617 <sup>j</sup>	-0.0113	-0.0043	-0.0193	0.04	0.17
$E_{disp}^{(22)}$	-0.00238	-0.0344	-0.0275	-0.0795	-0.46	-0.21 <sup>l</sup>
$E_{exch-disp}^{(20)}$	0.00103 <sup>j</sup>	0.0053	0.0246	0.0133	0.36	0.34 <sup>m</sup>
$E_{int}^{n}$	-0.02170 <sup>o</sup>	-0.1582	-0.1627	-0.4688	-5.49	-10.60
Empirical	-0.02176 <sup>p</sup>	-0.353 <sup>q</sup>	-0.1571 <sup>r</sup>	-0.47 <sup>s</sup>	-5.4±0.7 <sup>t</sup>	-11.2 <sup>u</sup>
Supermolecular <sup>v</sup>	-0.02160 <sup>w</sup>	-0.143 <sup>x</sup>			-4.56 <sup>y</sup>	
					-5.09 <sup>z</sup>	
					-5.1 <sup>*</sup>	

<sup>s</sup>Hutson, Ref. [91]

<sup>t</sup>Curtiss, Frurip, and Blander, Ref. [92].

<sup>u</sup>Sukhodub, Ref. [93].

<sup>v</sup>All supermolecular calculations cited here are CP corrected. Some of those calculations are for a slightly different geometry than the SAPT calculations.

<sup>w</sup>*spdfgh* MR-CI calculation by Vos, van Lenthe, and van Duijneveldt, Ref. [94].

<sup>x</sup>*spdf* MBPT4 calculation by Sadlej and Dierksen, Ref. [95].

<sup>y</sup>*spdf* MBPT4 calculation by Frisch *et al.*, Ref. [96].

<sup>z</sup>MBPT2 calculation by Corongiu and Clementi, Ref. [97].

<sup>\*</sup>*spdfg* MBPT4 calculation by Feller, Ref. [98].