Symmetry-adapted perturbation theory of nonadditive three-body interactions in van der Waals molecules. I. General theory

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Symmetry-adapted perturbation theory of pairwise nonadditive interactions in trimers is formulated, and pure three-body polarization and exchange components are explicitly separated out. It is shown that the three-body polarization contributions through the third order of perturbation theory naturally separate into terms describing the pure induction, mixed induction–dispersion, and pure dispersion interactions. Working equations for these components in terms of molecular integrals and linear and quadratic response functions are derived. These formulas have a clear, partly classical, partly quantum mechanical, physical interpretation. The asymptotic expressions for the second- and third-order three-body polarization contributions through the multipole moments and (hyper)polarizabilities of the isolated monomers are reported. Finally, assuming the random phase approximation for the response functions, explicit orbital formulas for the three-body polarization terms are derived. The exchange terms are also classified, and the simplest approximations (neglecting intramonomer correlation effects) are written as explicitly connected commutator expressions involving second-quantized operators. The corresponding orbital formulas are also reported. © 1995 American Institute of Physics.

I. INTRODUCTION

One of the frequent assumptions in molecular physics is the pairwise additivity of intermolecular interactions. Before the advent of modern simulation techniques this assumption was crucial for a tractable treatment of bulk properties of matter. It was also made because very little quantitative information about departures from nonadditivity was available. Although the nonadditive effects are much smaller than the additive ones, it is now generally accepted that the nonadditivity of interactions is the key to understanding many features of weakly interacting molecules in gases, liquids, and solids. Axilrod and Teller and Muto were the first who pointed out the possible importance of nonadditivity in interactions between spherically symmetric atoms, and who derived an analytical expression for the long-range part of the three-body force. Löwdin proved that nonadditive effects are responsible for the deviations from the Cauchy relations between elastic constants of ionic solids. Later, it was shown that these effects strongly affect higher-order virial coefficients as well as the structure and thermodynamic properties of homogeneous and heterogeneous clusters of atoms and molecules. Nonadditive interactions are also important in modeling atom–surface interactions. For a more detailed discussion of the role of many-body effects in the description of bulk properties of matter we refer the reader to Refs. 10 and 11.

Recent advances in scattering techniques allow very detailed structural and dynamical studies of small clusters of atoms and molecules. In particular, recently it has become possible to record the microwave and far-infrared spectra of Ar2–HCl (Ref. 13) and microwave spectra of Ar2–HF (see also Ref. 16 for a review). These spectra could not be fully explained using the pairwise additivity assumption, although the empirical two-body potentials for Ar–HCl, Ar–HF, and Ar2 (Ref. 21) are known very accurately. Also the red shift of the fundamental band of HF in the Ar matrix could not be reproduced from five-dimensional dynamical calculations on the two-body Ar–HF potential. Since nearly exact quantum Monte Carlo calculations for large clusters are now becoming feasible any information on collective many-body effects would be useful in structural and dynamical studies of these systems.

In principle, nonadditive three-body potentials for simple systems like Ar2–HCl or Ar2–HF could be extracted from the experimental data by adjusting the parameters to reproduce the results of measurements. For two-body potentials this procedure has been applied with success and produced highly accurate potentials. In general, however, such an approach requires some a priori assumptions on the functional form of the potential and the long-range van der Waals constants. These, in turn, can be obtained from a...
consistent perturbation theory including major long-range and exchange effects.

Until recently, the perturbation theory of nonadditive interactions was mainly based on the Rayleigh–Schrödinger polarization treatment (neglecting the intramolecular electron exchange) coupled with the multipole expansion of the interaction operator (neglecting, in turn, charge overlap and damping effects). However, as pointed out by O'Shea and Meath, the charge overlap effects modify both the radial and angular dependence of the interaction energy. This shows that the multipole-expanded representation of the nonadditive contributions may be a very poor approximation to the true three-body effect. Although a consistent symmetry-adapted perturbation theory of nonadditive three-body interactions has been formulated in 1974, only the simplest many-body contributions to the interaction energy have been implemented for many-electron systems: the first-order (Heitler–London) nonadditivity, the second-order induction nonadditivity, and the third-order dispersion nonadditivity, all with neglect of the effects of the intramonomer electronic correlation. In addition, Bulski and Chalasinski considered the second-order exchange-dispersion nonadditivity in the system of three helium atoms.

The second-order exchange nonadditivity has been also considered by Tachikawa and Iguchi. However, these authors neglected all terms cubic in the intermolecular overlap integrals. This approximation has been shown to be very crude for the Heitler–London nonadditivity, and it is not expected to work well for the second-order exchange contributions.

Let us mention that Chalasinski and collaborators developed an approach to study nonadditive three-body interactions that combines the supermolecule Möller–Plesset theory with the simplest approximations to the induction and dispersion nonaddativities. This approach has been applied to characterize interactions in various trimers. (see also Ref. 42 for a review). It is also worth noting that several supermolecule calculations have been reported for atomic, molecular, and metallic clusters. Recently, the many-electron formulation of the symmetry-adapted perturbation theory (SAPT) of two-body interactions has been developed. In this approach all physically important contributions to the potential, such as electrostatics, exchange, induction, and dispersion are identified and computed separately. By making a perturbation expansion in the intermolecular interaction as well as in the intramolecular electronic correlation, it is possible to sum the correlation contributions to the different physical effects only as far as necessary. The SAPT approach does not use the multipole expansion, so all charge penetration (damping) effects are automatically included. Since various contributions to the interaction energy show a different dependence on the intermolecular distance $R$, they can be fitted separately, with adjustable and physically interpretable parameters. This method has been applied to determine interaction potentials for the He–K$^+$, He–Na$^+$, Ar–H$_2$, He–HF, He–C$_2$H$_2$, He–CO, and Ar–HF (Ref. 70) systems (see Ref. 71 for a recent review of SAPT theory and applications). In most cases, excellent agreement is achieved when compared with the accurately determined (semi)empirical potentials available for these systems. The SAPT potentials have been used to generate far- and near-infrared spectra of Ar–H$_2$, and the near-infrared spectra of He–HF, He–C$_2$H$_2$, and He–CO. In general, the resulting line positions are in very good agreement with the experimental data (see Ref. 74 for a review of dynamical calculations). Also state-to-state integral cross sections and total differential cross sections for He–HF agree rather well with the available experimental data, suggesting that SAPT maintains good accuracy both at short and large distances.

Since the SAPT theory of two-body interactions is well developed, it is natural to generalize it to nonadditive three-body interactions. It is the aim of this paper to report such a generalization. The plan of this paper is as follows. In Sec. II we formulate the triple perturbation theory of interactions in trimers, and show how the pure three-body effects can be separated out. Also presented in this section are expressions for the polarization contributions in terms of molecular integrals and linear and quadratic response functions. These expressions have a clear, partly classical, partly quantum mechanical, physical interpretation. Finally, assuming some approximations to the response functions, they can be used in actual calculations. The exchange terms are also classified, and the simplest approximations (neglecting intramonomer correlation effects) are written as commutator expressions involving second-quantized operators. In Sec. III we present the multipole-expanded formulas for the polarization contributions derived in Sec. II. Finally, in Sec. IV we shortly summarize the present work. Explicit orbital formulas (ready for computer programming) for the polarization and exchange contributions derived in the present paper are reported in Appendices A and B, respectively. In a forthcoming paper we present some illustrative applications of this theory to a system of current experimental interest, Ar$_2$–HF.

II. TRIPLE PERTURBATION THEORY OF INTERMOLECULAR INTERACTIONS IN CLOSED-SHELL TRIMERS

We consider the interaction of three closed-shell systems $A$, $B$, and $C$. The total Hamiltonian of the trimer $ABC$ can be conveniently written as

$$H = H_0 + \xi V^{AB} + \eta V^{BC} + \chi V^{CA},$$  

(1)

where $H_0 = H^A + H^B + H^C$ is the sum of Hamiltonians of the isolated monomers, the operator $V^{XY}$ collects all Coulombic interactions between electrons and nuclei of monomers $X$ and $Y$, and the parameters $\xi$, $\eta$, and $\chi$ have the physical value equal to unity. The interaction energy of the trimer can be written as

$$E_{\text{int}}(\xi, \eta, \chi) = \langle \Psi_0 | (\xi V^{AB} + \eta V^{BC} + \chi V^{CA}) | \Psi(\xi, \eta, \chi) \rangle,$$

(2)

where $\Psi_0 = \Psi_{0}^A \Psi_{0}^B \Psi_{0}^C$ is the ground state wave function of the unperturbed Hamiltonian $H_0$, and $| \Psi(\xi, \eta, \chi) \rangle$ denotes the ground state wave function of the monomer $X$. We assume that the wave function of the trimer $\Psi(\xi, \eta, \chi)$ satisfies the intermediate normalization condition,

$$\langle \Psi_0 | \Psi(\xi, \eta, \chi) \rangle = 1.$$

(3)
This function is a solution of the parametrized Schrödinger equation for the trimer,

\[(H_0 - E_0)\Psi(\zeta, \eta, \chi) = \left[ E_{\text{int}}(\zeta, \eta, \chi) - \zeta V^{AB} - \eta V^{BC} - \chi V^{CA} \right] \Psi(\zeta, \eta, \chi), \tag{4}\]

where \(E_0 = E_0^A + E_0^B + E_0^C\) is the ground state energy of \(H_0\) and \(E_0^A\) is the ground state energy of the monomer \(X\). Equations (2) and (4) form a convenient starting point for a Rayleigh–Schrödinger (RS) type perturbation expansion (polarization expansion)\(^{60}\). Although at low order the polarization expansion is known not to reproduce the exchange components of the interaction energy,\(^{77-79}\) this method plays an important role in the theory of intermolecular forces.\(^{71}\) First, the low-order terms in the energy expansion have a clear, and well established physical meaning,\(^{71}\) and provide rigorous definitions of such important concepts as two-body electrostatic, induction, and dispersion interactions. Second, the symmetry-adapted perturbation theories\(^{71}\) provide exchange contributions which can be added to the polarization terms. For the two-body interactions this approach gives an accurate representation of the interaction energy in various regions of the configuration space (see Ref. 71 for a review).

The parametrized interaction energy and wave function, \(E_{\text{int}}(\zeta, \eta, \chi)\) and \(\Psi(\zeta, \eta, \chi)\), are expanded as power series in \(\zeta\), \(\eta\), and \(\chi\),

\[
E_{\text{int}}(\zeta, \eta, \chi) = \sum_{i,j,k} \zeta^i \eta^j \chi^k E_{\text{pol}}^{(ijk)},
\]

\[
\Psi(\zeta, \eta, \chi) = \sum_{i,j,k} \zeta^i \eta^j \chi^k \Psi_{\text{pol}}^{(ijk)},
\tag{5}\]

where \(E_{\text{pol}}^{(ijk)}\) and \(\Psi_{\text{pol}}^{(ijk)}\) denote the polarization energy and wave function of \(i\)th order in \(V^{AB}\), \(j\)th order in \(V^{BC}\), and \(k\)th order in \(V^{CA}\). We assume that \(E_{\text{pol}}^{(000)} = 0\) and \(\Psi_{\text{pol}}^{(000)} = \Psi_0\). The energy and wave function corrections, \(E_{\text{pol}}^{(ijk)}\) and \(\Psi_{\text{pol}}^{(ijk)}\), can be obtained from triple perturbation theory equations\(^{33,35}\)

\[
(H_0 - E_0)\Psi_{\text{pol}}^{(ijk)} = - V^{AB} \Psi_{\text{pol}}^{(i-1,j,k)} - V^{BC} \Psi_{\text{pol}}^{(i,j-1,k)} - V^{CA} \Psi_{\text{pol}}^{(i,j,k-1)}
+ \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} E_{\text{pol}}^{(lmn)} \Psi_{\text{pol}}^{(i-1,j-1,m,k-n)}, \tag{6}\]

where \(\Psi_{\text{pol}}^{(ijk)}\) and \(E_{\text{pol}}^{(ijk)}\) are zero if one of the indices \(i\), \(j\), and \(k\) is negative.

As discussed above the polarization expansion neglects the exchange effects. The exchange contributions can be incorporated into the theory by a suitable symmetry-adaptation. Various symmetry-adapted perturbation theories have been studied in the past.\(^{55,56,71}\) Our experience\(^{80,57,79}\) for the two-body interactions suggests that the simplest symmetrized Rayleigh–Schrödinger (SRS) perturbation theory\(^{80,57}\) shows satisfactory convergence properties and can be applied to many-electron systems in practice. In the SRS theory the exchange contributions are obtained by introducing the antisymmetrization into the energy expression, keeping Eqs. (4) and (6) intact. The appropriate energy expression is

\[
E_{\text{int}}(\zeta, \eta, \chi) = \frac{\langle \Psi_0 | (\zeta V^{AB} + \eta V^{BC} + \chi V^{CA}) \Psi(\zeta, \eta, \chi) \rangle}{\langle \Psi_0 | \Psi(\zeta, \eta, \chi) \rangle}, \tag{8}\]

where \(\mathcal{A}\) is the full antisymmetrizer of the trimer. Note that \(E_{\text{int}}(\zeta, \eta, \chi)\) and \(E_{\text{int}}(\zeta, \eta, \chi)\) are two different functions of the parameters \(\zeta\), \(\eta\), and \(\chi\), possibly equal for \(\zeta = \eta = \chi = 1\). Equation (8) can be represented as a power series in \(\zeta\), \(\eta\), and \(\chi\),

\[
E_{\text{int}}(\zeta, \eta, \chi) = \sum_{i,j,k} \zeta^i \eta^j \chi^k E_{\text{pol}}^{(ijk)}, \tag{9}\]

where \(E^{(000)} = 0\), and \(E^{(ijk)}\), \((i,j,k) \neq (0,0,0)\), is given by

\[
E^{(ijk)} = N^{ABC} \left[ \langle \Psi_0 | V^{AB} \mathcal{A} \Psi^{(i-1,j,k)} \rangle \right. \\
+ \langle \Psi_0 | V^{BC} \mathcal{A} \Psi^{(i,j-1,k)} \rangle \left. + \langle \Psi_0 | V^{CA} \mathcal{A} \Psi^{(i,j,k-1)} \rangle \right]
- \left. N^{ABC} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} E^{(lmn)} \langle \Psi_0 | \mathcal{A} \Psi^{(i-1,j-1,m,k-n)} \rangle. \tag{10}\right.\]

\[N^{ABC} = (\Psi_0 \mathcal{A} \Psi_0)^{-1}\] and the prime on the summation symbol reminds us that the term with \((lmn) = (ijk)\) is excluded from the summation.

The exchange contributions to the interaction energy are defined by

\[
E^{(ijk)}_{\text{exch}} = E^{(ijk)} - E^{(ijk)}_{\text{pol}}. \tag{11}\]

To derive a closed expression for \(E^{(ijk)}_{\text{exch}}\) it is useful to express the total antisymmetrizer of the trimer as

\[
\mathcal{A} = C \mathcal{A}^A \mathcal{A}^B \mathcal{A}^C (1 + \mathcal{P}), \tag{12}\]

where \(C = (N_A + N_B + N_C)! / (N_A! N_B! N_C!)\), \(N_X\) is the number of electrons of the monomer \(X\), \(\mathcal{A}^X\) is the antisymmetrizer for the monomer \(X\), and the operator \(\mathcal{P}\) collects all intermolecular exchanges,

\[
\mathcal{P} = p^{AB} + p^{BC} + p^{CA} + p^{ABC} + p'. \tag{13}\]

The operators \(p^{XY}\) and \(p^{XYZ}\) are explicitly given by

\[
p^{XY} = - \sum_{i \in X} \sum_{j \in Y} P_{ij}, \tag{14}\]

and

\[
p^{XYZ} = \sum_{i \in X} \sum_{j \in Y} \sum_{k \in Z} (P_{ijk} + P_{jik}), \tag{15}\]

where \(P_{ij}\) interchanges the spin and space coordinates of electrons \(i\) and \(j\), \(P_{ijk}\) permutes cyclically the spin and space coordinates of electrons \(i, j, k\), while \(p'\) collects all higher exchanges between the interacting subsystems. Using Eqs. (7), (10), (11), and the representation (12) of \(\mathcal{A}\), one finds, since \(N^{ABC} = C^{-1} \langle \Psi_0 | (1 + \mathcal{P}) \Psi_0 \rangle^{-1}\) and \(\mathcal{A}^X \mathcal{A}^B \mathcal{A}^C \Psi^{(ijk)} = \Psi^{(ijk)}_{\text{pol}}\), that the explicit formula for

\[E^{(ijk)}_{\text{exch}}\] is given by

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while all contributions $E_{\text{pol}}^{(100)}$, $E_{\text{pol}}^{(010)}$, and $E_{\text{pol}}^{(001)}$ are purely additive, i.e.,

$$E_{\text{pol}}^{(100)} = E_{\text{pol}}^{(100)}(2,3),$$

$$E_{\text{pol}}^{(010)} = E_{\text{pol}}^{(010)}(2,3),$$

$$E_{\text{pol}}^{(000)} = E_{\text{pol}}^{(000)}(2,3).$$

The equivalents of Eqs. (20) and (21) are also valid for the polarization wave functions $\Psi_{\text{pol}}^{(i,j,k)}$.

By contrast, the exchange contributions $E_{\text{exch}}^{(000)}$, $E_{\text{exch}}^{(010)}$, and $E_{\text{exch}}^{(000)}$ are not necessarily additive, since in general the antisymmetrizer will interchange the coordinates of electrons belonging to all three monomers. The two-body contribution to $E_{\text{exch}}^{(000)}$ can be easily identified by moving in Eq. (16) the third monomer to infinity, i.e.,

$$E_{\text{exch}}^{(000)}(2,3) = \lim_{R_{BC} \to \infty} \lim_{R_{CA} \to \infty} E_{\text{exch}}^{(000)} R_{AB} = \text{const.}$$

Since the polarization wave functions $\Psi_{\text{pol}}^{(000)}$ defining $E_{\text{exch}}^{(000)}$ are purely additive, i.e., $\Psi_{\text{pol}}^{(000)} = \Psi_{\text{pol}}^{(000)}(2,3)$, the two-body term as defined by Eq. (22) is equal to $E_{\text{exch}}^{(000)}$ as defined by the SRS theory of two-body interactions. Thus, to extract the pure three-body contribution to $E_{\text{exch}}^{(000)}$ one has to subtract the $E_{\text{exch}}^{(000)}(3,3)$ term of the two-body SRS theory. The expression for $E_{\text{exch}}^{(000)}(3,3)$ follows then directly by subtraction. If we neglect all terms quartic and of higher order in the intermolecular overlap densities, the formula for $E_{\text{exch}}^{(000)}(3,3)$ can be written as

$$E_{\text{exch}}^{(000)}(3,3) = \langle \Psi_0 | V^{AB}(Q^{AB} - \langle Q^{AB} \rangle) | \Psi_{\text{pol}}^{(i-1,00)} \rangle - \sum_{i=0}^{i-1} E_{\text{pol}}^{(i)} \langle \Psi_0 | Q^{AB} | \Psi_{\text{pol}}^{(i-1,00)} \rangle,$$

where $Q^{AB} = P - PA$ [recall that $P$ is defined by Eq. (18)] and $\langle Q^{AB} \rangle = \langle \Psi_0 | Q^{AB} \Psi_0 \rangle$.

B. Classification of three-body contributions to the interaction energy

The expressions for the nonadditive three-body contributions derived in the previous section involve in general exact wave functions of the monomers and the reduced resolvent of the zeroth-order Hamiltonian $H_0$. Since these quantities are not available for any but one- and two-electron molecules, one has to formulate a many-electron theory that systematically treats intramonomer correlation effects. This can be done by generalizing the coupled-cluster approach of Refs. 48 and 50. Another possibility, widely explored in the case of two-body interactions, is to express the perturbation theory corrections to the interaction energy through the properties of the isolated monomers. In the present paper the former approach will be used to derive working expressions for the exchange contributions, the latter will be followed to find formulas for the polarization terms.

The definitions of the nonadditive contributions derived in the previous section involve nonsymmetric operators, like $H_0$ and $V^{AB}$. These operators do not include all electrons in a fully symmetric way, and in fact $H_0$ and $V^{AB}$ act in a larger space than the fully antisymmetric Hilbert space $\mathcal{H}_{ABC}$ of
the trimer \( ABC \). To use these operators we have to consider the space \( \mathcal{H}_A \otimes \mathcal{H}_B \otimes \mathcal{H}_C \), i.e., the tensor product of antisymmetric Hilbert space \( \mathcal{H}_A \), \( \mathcal{H}_B \), and \( \mathcal{H}_C \) for the molecules \( A \), \( B \), and \( C \). The permutations of electrons between the interacting molecules lead in general to wave functions which do not belong to the space \( \mathcal{H}_A \otimes \mathcal{H}_B \otimes \mathcal{H}_C \). We define the one-electron space \( \mathcal{I} \) as the space spanned by the union of all three atomic bases associated with the three monomers in the trimer. The basis of the space \( \mathcal{I} \) includes functions centered on all atoms in the trimer and, consequently, will be referred to as the trimer-centered basis. We assume that the same one-electron space \( \mathcal{I} \) is used to construct the three Hilbert spaces \( \mathcal{H}_X \), \( X = A \), \( B \), and \( C \) [i.e., \( \mathcal{H}_X = \mathcal{I} \otimes \mathcal{N}_X = \mathcal{I} \otimes \cdots \otimes \mathcal{I} \) (\( N_X \) factors)]. In such case every fully antisymmetric function from \( \mathcal{H}_{ABC} \) can be expanded in terms of functions from \( \mathcal{H}_A \otimes \mathcal{H}_B \otimes \mathcal{H}_C = \mathcal{I} \otimes \mathcal{I} \otimes \cdots \otimes \mathcal{I} \) (\( N_A+N_B+N_C \) factors). Thus, \( \mathcal{H}_{ABC} \subseteq \mathcal{H}_A \otimes \mathcal{H}_B \otimes \mathcal{H}_C \), since \( \mathcal{H}_{ABC} \) is obtained by projection of \( \mathcal{H}_A \otimes \mathcal{H}_B \otimes \mathcal{H}_C \) with \( \mathcal{I} \), and all physical solutions of the Schrödinger equation belong to \( \mathcal{H}_A \otimes \mathcal{H}_B \otimes \mathcal{H}_C \).

Summation over repeated lower and upper indices is implied throughout the rest of this paper (the Einstein convention). From now on we shall always assume that the indices \( a, a'; \ldots \), \( b, b'; \ldots \), and \( c, c'; \ldots \) will denote occupied spatial orbitals of the molecule \( A, B \), and \( C \), respectively. The indices \( \alpha, \alpha'; \ldots \), \( \beta, \beta'; \ldots \), and \( \gamma, \gamma'; \ldots \) will denote virtual spin orbitals of the molecules \( A, B \), and \( C \), respectively. The indices \( a, a'; \ldots \), \( b, b'; \ldots \), and \( c, c'; \ldots \) will label virtual spatial orbitals of the molecules \( A, B \), and \( C \), respectively. The indices \( \alpha, \alpha'; \ldots \), \( \beta, \beta'; \ldots \), and \( \gamma, \gamma'; \ldots \) will label virtual spin orbitals of the molecules \( A, B \), and \( C \), respectively. The indices \( a, a'; \ldots \), \( b, b'; \ldots \), and \( c, c'; \ldots \) will label virtual spatial orbitals of the molecules \( A, B \), and \( C \), respectively. The indices \( \alpha, \alpha'; \ldots \), \( \beta, \beta'; \ldots \), and \( \gamma, \gamma'; \ldots \) will label virtual spin orbitals of the molecules \( A, B \), and \( C \), respectively.

The strings of equal number of conventional creation and annihilation operators acting in \( \mathcal{H}_A \), \( \mathcal{H}_B \), and \( \mathcal{H}_C \) will be denoted by

\[
a_{\alpha_1 \cdots \alpha_n} = a_{\alpha_1} \cdots a_{\alpha_n},\quad a_{\pm (\alpha_1 \cdots \alpha_n)} = a_{\alpha_1} \cdots a_{\alpha_n} \pm a_{\alpha_n} \cdots a_{\alpha_1},
\]

\[
b_{\mu_1 \cdots \mu_m} = b_{\mu_1} \cdots b_{\mu_m},\quad b_{\pm (\mu_1 \cdots \mu_m)} = b_{\mu_1} \cdots b_{\mu_m} \pm b_{\mu_m} \cdots b_{\mu_1},
\]

\[
c_{\xi_1 \cdots \xi_p} = c_{\xi_1} \cdots c_{\xi_p},\quad c_{\pm (\xi_1 \cdots \xi_p)} = c_{\xi_1} \cdots c_{\xi_p} \pm c_{\xi_p} \cdots c_{\xi_1},
\]

respectively. We will employ the same notation for analogous operators acting in \( \mathcal{H}_A \otimes \mathcal{H}_B \otimes \mathcal{H}_C \), although these operators should be written as tensor products, i.e., \( a_{\alpha_1 \cdots \alpha_n} \otimes 1_B \otimes 1_C \), \( 1_A \otimes b_{\mu_1 \cdots \mu_m} \otimes 1_C \), and \( 1_A \otimes 1_B \otimes c_{\xi_1 \cdots \xi_p} \).

Alternatively, one may view the operators \( a_{\alpha_1 \cdots \alpha_n} \), \( b_{\mu_1 \cdots \mu_m} \), and \( c_{\xi_1 \cdots \xi_p} \) as associated with different sets of variables, so that they must commute

\[
[a_{\alpha_1 \cdots \alpha_n} b_{\mu_1 \cdots \mu_m} c_{\xi_1 \cdots \xi_p}] = 0,
\]

\[
[a_{\alpha_1 \cdots \alpha_n} c_{\xi_1 \cdots \xi_p}] = 0,
\]

We assume that the spin-orbital basis sets \( \{ \phi_a \} \), \( \{ \phi_b \} \), and \( \{ \phi_c \} \) used to define \( a_\alpha \), \( b_\mu \), and \( c_\xi \) are orthonormal. The operators \( a_{\alpha_1 \cdots \alpha_n} b_{\mu_1 \cdots \mu_m} c_{\xi_1 \cdots \xi_p} \) multiply according to the rules given by Eqs. (15)–(17) of Ref. 50.

The operators \( H^\alpha \), \( X = A, B, \) or \( C \), can be represented by the standard second-quantized expressions, while the intermolecular interaction operator \( V_{AB} \),

\[
V_{AB} = \sum_{i \in A} V_B(r_i) + \sum_{j \in B} V_A(r_j) + \sum_{i \in A} \sum_{j \in B} r_{ij}^{-1} + V_{AB}^0,
\]

where \( V_{AB}^0 \) is the constant nuclear repulsion term. Further,

\[
u_{ak} = \langle \phi_a(1) | \phi_k(2) | r_{12} \rangle \langle \phi_k(1) | \phi_a(2) \rangle
\]

and \( v_{ak} = (\phi_a(1) | \phi_k(2)) \) is a matrix element of the electrostatic potential of all the nuclei of molecule \( X \). Similar expressions for \( V^B_C \) and \( V^C_A \) can be easily found by an obvious permutation of symbols in Eq. (29).

We also need the second-quantized expressions for the exchange operators \( P^A_B \) and \( P^A_BC \) appearing in the expressions for the exchange contributions. Making use of the assumption that the spin-orbital basis sets \( \{{\phi}_a\} \), \( \{{\phi}_b\} \), and \( \{{\phi}_c\} \) span the same linear space \( \mathcal{I} \), one can show that the operator \( P^A_BC \) can be represented in the following second-quantized form:

\[
P^A_BC = -S^B_{a\mu} a_{\mu} b_a^\dagger + S^C_{a\mu} a_{\mu} b_a^\dagger c_{\xi}^\dagger c_{\xi}^\dagger + S^A_{a\mu} a_{\mu} b_a^\dagger c_{\xi}^\dagger c_{\xi}. \tag{31}
\]

where \( S_{a\mu}^A \) is the intermolecular overlap integral. \( S_{a\mu}^A = (\phi_a | \phi_\mu) \). The operator \( P^A_BC \), in turn, can be written as

\[
P^A_BC = (S^A_{a\mu} S_{\xi}^B + S^A_{a\mu} S_{\xi}^C) a_{\mu} b_a^\dagger c_{\xi}^\dagger c_{\xi}. \tag{32}
\]

Similar expressions for \( P^B_C \) and \( P^C_A \) can be easily obtained from Eq. (31) by permuting symbols pertaining to monomers \( A, B, \) and \( C \). Equations (31) and (32) can be proved by verifying that the matrix elements of \( P^A_B \) and \( P^A_BC \) in the basis of products of Slater determinants are the same as the matrix elements of the first-quantized operators. Note that Eqs. (31) and (32) do not hold when finite monomer-centered basis sets are used, i.e., when the orbital basis sets used to construct \( \mathcal{H}_A \), \( \mathcal{H}_B \), and \( \mathcal{H}_C \) are localized on monomers \( A, B, \) and \( C \), respectively.

In the following derivations we will frequently use the linear and quadratic response functions (polarization propagators), denoted by \( \Pi^{\lambda\lambda'}_{\alpha\alpha'}(\omega) \) and \( \Pi^{\lambda\lambda'}_{\alpha\alpha'}(\omega_1, \omega_2) \), respectively. The linear response function is defined for the monomer \( A \) by the equation

\[
\Pi^{\lambda\lambda'}_{\alpha\alpha'}(\omega) = -\langle \Psi_0^A | a_{\lambda} \hat{R}^A(\omega) a_{\alpha}^\dagger | \Psi_0^A \rangle \tag{33}
\]

where the frequency-dependent resolvent operator \( \hat{R}^A(\omega) \) is defined as
Thus, in this particular case
\begin{equation}
\pi^{(2)}(\omega,\omega_2) = 2 \text{Re} \langle \Psi_0^A|\hat{A}^2\hat{A}^2|\Psi_0^A(\omega,\omega_2) \rangle - (1 \rightarrow 2), \tag{36}
\end{equation}

where
\begin{equation}
\rho^A_\omega = \langle \Psi_0^A|a^\dagger_\omega a^\dagger_\omega|\Psi_0^A \rangle,
\end{equation}

and (1→2) denotes three additional terms with all symbols with indices 1 and 2 interchanged (including those with \(\kappa_1,\lambda_1,\kappa_2,\kappa_2\)). [Note that in Ref. 85 the response functions of Eqs. (33) and (36) are denoted by \(\langle (a^\dagger_\omega a^\dagger_\omega) \rangle_\omega \) and \(\langle (a^\dagger_\omega a^\dagger_\omega) \rangle_{x,y,z} \), respectively.] In the next section we will also frequently use the operator \(\Omega^{X}_Y\) of the exact electro-static field of the unperturbed monomer \(X\) acting on electrons of the monomer \(Y\). This operator is explicitly defined by
\begin{equation}
\Omega^{X}_Y = \sum_{i=1}^{N_Y} \omega_X(r_i), \tag{37}
\end{equation}

where
\begin{equation}
\omega_X(r_i) = v_X(r_i) + \int \rho_X(r_i) r_{ij}^{-1}dr_j.
\end{equation}

and \(\rho_X(r_i)\) is the electron density of the monomer \(X\). The second-quantized equivalent of Eq. (37), e.g., \(Y = B\) and \(X = A\), is given by
\begin{equation}
\Omega^{X}_{Y} = \langle (a^\dagger_\omega a)_{\mu} \rangle_{\omega} + \langle (a^\dagger_\omega a)_{\mu} \rangle_{x,y,z} \rho^A_{\omega}.
\end{equation}

To simplify further discussion we shall occasionally refer to the energy corrections \(E^{(n)}(3,3)\) of the total \(n\)th order in the nuclear and electrostatic fields of monomer \(X\) and \(Y\), and \(V^B_C \) and \(V^{BC}\), respectively:
\begin{equation}
E^{(n)}(3,3) = \sum_{i,j,k=0} E^{(ijk)}(3,3). \tag{40}
\end{equation}

### 1. Polarization contributions

The electrostatic energy \(E^{(1)}_{\text{pol}}\) is additive, so the first nonadditive contribution is given by the second-order term,
\begin{equation}
E^{(2)}_{\text{pol}}(3,3) = E^{(10)}_{\text{pol}} + E^{(10)}_{\text{pol}} + E^{(10)}_{\text{pol}}, \tag{41}
\end{equation}

where, e.g., \(E^{(10)}_{\text{pol}}\) is explicitly given by
\begin{equation}
E^{(10)}_{\text{pol}} = 2 \text{Re} \sum_{m=0}^1 \frac{\langle \Psi_0^A|V^{AB}\Psi^A_0 \Psi^B_m \Psi^C_0 \rangle \langle \Psi^A_0 \Psi^B_m \Psi^C_0 |V^{BC}\Psi_0 \rangle}{E_0^A - E_0^B}.
\end{equation}

This sum-over-states expression can be conveniently rewritten as
\begin{equation}
E^{(10)}_{\text{pol}} = 2 \text{Re} \langle \Psi_0^A|\Omega^{AB} \Psi_0^A \rangle = 2 \text{Re} \langle \Psi_0^A|\Omega^{BC} \Psi_0^A \rangle,
\end{equation}

where \(\Omega^{AB}\) is the induction operator defined as in Ref. 85. Equation (43) clearly shows that \(E^{(10)}_{\text{pol}}\) represents the three-body induction term corresponding to the interaction of the electrostatic field of the molecule \(C\) with the molecule \(B\) polarized by the electrostatic field of \(A\). Thus, in this particular case \(E^{(10)}_{\text{pol}} = E^{(10)}_{\text{ind}}\) and \(E^{(10)}_{\text{ind}}(3,3) = E^{(10)}_{\text{ind}}(3,3)\). In the multipole approximation this contribution can be interpreted as the result of the interaction of permanent moments of monomer \(C\) with moments induced on monomer \(B\) by the electrostatic field of the monomer \(A\). Using the second-quantized representation of \(V^{AB}\), Eq. (29), a similar representation of \(V^{BC}\), and Eqs. (37), (38), and (33), one can rewrite the sum-over-states expression (42) in terms of the linear response function,
\begin{equation}
E^{(10)}_{\text{ind}} = \langle (a^\dagger_\omega a^\dagger_\omega)_{\mu} | \Omega^{AB} \Psi_0 \rangle \Pi^{AB}_{\mu} (0).
\end{equation}

Similar expressions for \(E^{(11)}_{\text{ind}}\), etc., can be easily found by a proper permutation of symbols pertaining to monomers \(A, B, C\). For the interaction of three spherical symmetric atoms this contribution to the nonadditive potential was considered for the first time by Wojtala.\(\text{Ref. } 86\) and is sometimes referred to as Wojtala nonadditivity.

A similar analysis of the third-order energy is somewhat more complicated, because the number of terms to be considered increases. When classifying the third-order nonadditive polarization contributions we will follow as closely as possible a similar classification for the two-body case (cf. Sec. II B 2 of Ref. 71). Thus, the energy of induction interactions, \(E^{(3)}(3,3)\), is defined as that part of \(E^{(3)}(3,3)\) which can be obtained by complete neglect of the intermonomer correlation effects. The difference \(E^{(3)}_{\text{ind}}(3,3) - E^{(3)}_{\text{disp}}(3,3)\) represents all intermonomer correlation effects, and separates into contributions due to purely third-order dispersion interactions and to the coupling of the second-order dispersion interaction with the induction interaction,
\begin{equation}
E^{(3)}(3,3) = E^{(3)}_{\text{disp}}(3,3) + E^{(3)}_{\text{ind-disp}}(3,3) + E^{(3)}_{\text{ind-disp}}(3,3).
\end{equation}

Below, we report the definitions of these components in terms of the induction and dispersion operators and intermolecular interaction operators, and show how these contributions can be expressed through molecular integrals and response functions of the isolated monomers.

The dispersion nonadditivity \(E^{(3)}_{\text{disp}}(3,3)\) is due to the coupling of intermonomer pair correlations in subsystems \(XY\) and \(YZ\) via the intermolecular interaction operator \(V^{XY}\). This contribution can be conveniently expressed as a generalized Casimir–Polder formula,
For the interaction of three spherically symmetric atoms the third-order dispersion nonadditivity contains the famous Axilrod–Teller–Muto triple-dipole interaction.\(^1,2\)

The induction–dispersion contribution, in turn, can be interpreted as the energy of the (second-order) dispersion interaction of the monomer X with the monomer Y deformed by the electrostatic field of the monomer Z (note that we have six such contributions). In particular, when X = A, Y = B, and Z = C the corresponding induction–dispersion contribution is

\[
E_{\text{ind-disp}}^{(210)} = 2 \text{Re} \left( \hat{D}_{AB} \Psi_0 \left[ [V_{AB}^{\text{disp}}]_C \right] \Psi_0 \right)
\]

\[
+ \left\langle \hat{D}_{AB} \Psi_0 \left[ \Omega_C^{\text{disp}} \hat{D}_{AB} \right] \Psi_0 \right\rangle,
\]

(47)

where \(\hat{D}_{AB} = -\hat{R}_{AB}^{\text{disp}} V_{AB}^{\text{disp}} P_A^0 P_B^0\) is the dispersion operator defined as in Sec. II B of Ref. 71. \(\hat{R}_{AB}^{\text{disp}} = (H_A + H_B - E_0 - E_0 + P_A^0 P_B^0)^{-1} Q_{AB}^{\text{disp}} - \hat{R}_{AB}^{\text{disp}} P_A^0 P_B^0\), and \(Q_{AB}^{\text{disp}} = 1 - P_A^0 P_B^0\). Note the similarity between the above definition of \(E_{\text{ind-disp}}^{(210)}\) and the definition of the two-body induction–dispersion energy given by Eq. (25) of Ref. 71. In terms of response functions this contribution is given by

\[
E_{\text{ind-disp}}^{(210)} = -\frac{1}{4\pi} \left( \omega_C \right)_{\mu_1 \nu_1}^{\lambda_1 \kappa_1} \int_{-\infty}^{+\infty} \Pi_{\mu_1 \lambda_1 \kappa_1}^{\nu_1 \kappa_1} (-i \omega, 0) d\omega,
\]

(48)

where \(\Pi_{\mu_1 \mu_2 \lambda_1 \kappa_1}^{\nu_1 \kappa_1} (-i \omega, 0)\) is defined by Eq. (36). Similar expressions for \(E_{\text{ind-disp}}^{(210)}\), etc., can be easily found by a proper permutation of symbols pertaining to monomers A, B, and C.

The mechanism of the third-order three-body induction interactions is somewhat more complicated. It can be shown that one can distinguish three principal categories. The first mechanism is simply the interaction of permanent moments on the monomer C with the moments induced on B by the nonlinear (second-order) effect of the electrostatic potential of the monomer A plus contributions obtained by interchanging the roles of the monomers A and C. The corresponding contribution is

\[
E_{\text{ind}}^{(210)}(B \rightarrow A, C) = \left( i \hat{D}_{AB} \Psi_0 \left[ \Omega_C^{\text{disp}} \hat{D}_{AB} \right] \Psi_0 \right)
\]

\[
+ 2 \text{Re} \left( i \hat{D}_{AB} \Psi_0 \left[ \Omega_C^{\text{disp}} \hat{D}_{AB} \right] \Psi_0 \right).
\]

(49)

In terms of quadratic response function it takes the form

\[
E_{\text{ind}}^{(210)}(B \rightarrow A, C) = \frac{1}{2} \left( \omega_A \right)_{\mu_1 \mu_2}^{\nu_1 \nu_2} \left( \omega_C \right)_{\mu_2 \mu_3}^{\nu_2 \nu_3} \int \Pi_{\mu_1 \mu_2 \mu_3}^{\nu_1 \nu_2 \nu_3} (0, 0).
\]

(50)

Note that we have six contributions of this type corresponding to six possible permutations of the indices A, B, and C.

The second mechanism is the interaction between the multipole moments induced on A and C by the electrostatic potential of the monomer B. The induction energy component corresponding to this particular interaction will be denoted by \(E_{\text{ind}}^{(111)}(A \rightarrow B; C \rightarrow B)\), and can be written as

\[
E_{\text{ind}}^{(111)}(A \rightarrow B; C \rightarrow B) = 2 \text{Re} \left( i \hat{D}_{AB} \Psi_0 \left[ V_{\text{CA}} \hat{D}_{AB} \right] \Psi_0 \right)
\]

\[
+ 2 \text{Re} \left( \Psi_0 \left[ V_{\text{CA}} \hat{D}_{AB} \right] \Psi_0 \right).
\]

(51)

The corresponding expression in terms of linear response functions is

\[
E_{\text{ind}}^{(111)}(A \rightarrow B; C \rightarrow B) = \left( \omega_B \right)_{\mu_1 \mu_2}^{\nu_1 \nu_2} \int \Pi_{\mu_1 \mu_2}^{\nu_1 \nu_2} (0, 0).
\]

(52)

Since by definition \(E_{\text{ind}}^{(111)}(A \rightarrow B; C \rightarrow B) = E_{\text{ind}}^{(111)}(C \rightarrow B; A \rightarrow B)\), we have obviously three contributions of this kind.

The third mechanism corresponds to the interaction of multipole moments induced in monomers B and C by the electrostatic potentials of monomers A and B, respectively. The corresponding energy contribution, denoted by \(E_{\text{ind}}^{(210)}(A \rightarrow B; B \rightarrow C)\), is

\[
E_{\text{ind}}^{(210)}(A \rightarrow B; B \rightarrow C) = 2 \text{Re} \left( \hat{D}_{AB} \Psi_0 \left[ V_{\text{AB}} \hat{D}_{AB} \right] \Psi_0 \right)
\]

\[
+ 2 \text{Re} \left( \Psi_0 \left[ V_{\text{AB}} \hat{D}_{AB} \right] \Psi_0 \right).
\]

(53)

This term can be expressed in terms of linear response functions of monomers A and B as

\[
E_{\text{ind}}^{(210)}(A \rightarrow B; B \rightarrow C) = \left( \omega_B \right)_{\mu_1 \mu_2}^{\nu_1 \nu_2} \int \Pi_{\mu_1 \mu_2}^{\nu_1 \nu_2} (0, 0).
\]

(54)

Again we have six contributions of this type corresponding to six possible permutations of the indices A, B, and C.

Our classification of the third-order nonadditive polarization contributions is in agreement with the analysis of Stogryn\(^27\) based on the multipole expansion in the Cartesian form, although Stogryn includes the mixed induction–dispersion term into the third-order dispersion energy. It should be pointed out, however, that our definition for the third-order induction energy differs from the sum of the third-order induction energy contributions considered by Piecuch.\(^28,31,87\) Specifically, the second terms in Eqs. (51) and (53) are neglected by Piecuch, and his third-order nonadditivity cannot be expressed by the response functions of the monomers. Thus, also the formulas for the specific case of atom–atom–diatom interactions,\(^87\) as well as the numerical results for Ar\(_2\)–HF and Ar\(_2\)–HCl reported in Ref. 41, are not correct. In view of the above, the multipole expansion of the three-body dispersion energy (including the induction–dispersion term) as reported in Ref. 29 cannot be correct. Since the literature results in the spherical form are not entirely satisfactory, in Sec. III we report the multipole-expanded formulas for the three-body components considered in this section.

Although Eqs. (44), (46), (48), (50), (52), and (54) represent a reformulation of the theory reported in Sec. II, they give us useful insight into the physical nature of the nonadditive three-body interactions. Moreover, these expressions form a convenient starting point for computational considerations. At present the electron densities (needed to construct
the matrix elements of $\Omega_j^p$ and response functions can be accurately computed using powerful techniques developed in the 1980s (see, e.g., Refs. 85 and 88), so once the monomer properties are available, the three-body contributions can be easily obtained. It should be noted, however, that accurate calculations of the interaction energy components require the use of trimer-centered basis sets, so the expensive step of calculating the propagators must be repeated at each geometry. Since we are interested in the calculations of the full potential energy surfaces, the use of very advanced approximations to the polarization propagators would make the calculations prohibitively expensive. Therefore, in the present work we will use the response functions of the random phase approximation (RPA), also known as the time-dependent coupled-Hartree–Fock method. An analysis similar to that reported in Ref. 37 shows that the RPA approximations to $E_{\text{exch}}(3,3)$ and $E_{\text{ind}}(3,3)$ are fully included in the supermolecule Hartree–Fock nonadditivity $E_{\text{HF}}^{\text{mp}}(3,3)$. Since the RPA propagator is exact through the first order in the intramonomer electronic correlation, and since the induction–dispersion energy is a second-order intermonomer correlation effect, the two leading-order terms in the many-body perturbation expansion (with respect to the intramonomer electronic correlation) of the RPA induction–dispersion energy are fully included in the supermolecule MP3 nonadditivity $\Delta E(3)(3,3)$, while the two leading-order terms of the RPA dispersion energy are fully included in the MP4 nonadditivity $\Delta E(4)(3,3)$. The supermolecule results reported in Refs. 37 and 41 suggest that this level of the theory should produce results of sufficient accuracy to describe correctly three-body effects in atom–molecule systems. Explicit orbital formulas for $E_{\text{exch}}^{(0)}(3,3)$, $E_{\text{ind}}^{(0)}(3,3)$, $E_{\text{disp}}^{(3)}(3,3)$, and $E_{\text{ind}}^{(0)}(3,3)$ in the RPA approximation are reported in Appendix A.

### 2 Exchange contributions

The leading first-order exchange nonadditivity is given by the sum

$$E_{\text{exch}}^{(1)}(3,3) = E_{\text{exch}}^{(00)}(3,3) + E_{\text{exch}}^{(01)}(3,3) + E_{\text{exch}}^{(001)}(3,3),$$

and is equivalent to the Heitler–London nonadditivity,

$$E_{\text{HL}}^{(1)}(3,3) = \frac{\langle \Psi_0 | H \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} - E_{\text{HL}}^{(0)}(2,3) - E_0,$$

where $E_{\text{HL}}^{(1)}(2,3)$ is the Heitler–London energy corresponding to all two-body interactions in the trimer. Practical evaluation of Eqs. (55) or (56) is very difficult, even assuming the single exchange approximation (i.e., the neglect of all terms quartic and of higher order in the overlap integrals). When the intramonomer correlation effects are neglected the expression (55) can be handled using a suitable density matrix formalism. An even simpler alternative is to approximate $E_{\text{exch}}^{(1)}(3,3)$ by the Heitler–London nonadditivity computed with the Hartree–Fock (HF) wave functions for the monomers. It can be shown that this energy differs from the first-order exchange contribution evaluated with the HF wave functions by terms quartic in the intermolecular overlap integrals, provided that the full basis of the trimer is used. In the present work we will approximate the first-order exchange nonadditivity by the Heitler–London nonadditivity computed with complete neglect of intramonomer correlation effects, but to all orders in the overlap integrals. It should be noted that the intramonomer correlation effects strongly affect the two-body first-order exchange energies, and their incorporation for the three-body case may be necessary. Work in this direction is in progress.

The second-order exchange nonadditivity is given by

$$E_{\text{exch}}^{(2)}(3,3) = E_{\text{exch}}^{(200)}(3,3) + E_{\text{exch}}^{(020)}(3,3) + E_{\text{exch}}^{(002)}(3,3) + E_{\text{exch}}^{(110)}(3,3) + E_{\text{exch}}^{(101)}(3,3) + E_{\text{exch}}^{(011)}(3,3).$$

Assuming the single exchange approximation, the expressions for $E_{\text{exch}}^{(200)}$ and $E_{\text{exch}}^{(110)}$ follow from Eqs. (23) and (19), respectively,

$$E_{\text{exch}}^{(200)}(3,3) = \langle \Psi_0 | (V^{AB} - \langle V^{AB} \rangle) \rangle \times \langle Q^{AB} - \langle Q^{AB} \rangle \rangle \psi_{\text{pol}}^{(100)},$$

and $E_{\text{exch}}^{(110)}(3,3) = \langle \Psi_0 | (V^{BC} - \langle V^{BC} \rangle) \rangle \langle P - \langle P \rangle \rangle \psi_{\text{pol}}^{(100)}.$

Equation (58) has been derived for the first time by Bulski and Chalasinski for the case of three helium atoms. They also derived a formula for $E_{\text{exch}}^{(110)}$ but in their expression, Eq. (2.32) of Ref. 39, the renormalization terms $E_{\text{pol}}^{(100)}$ and $E_{\text{pol}}^{(010)}$ are missing. Very recently Eqs. (58) and (59) (with sign errors in the first terms) were reported in Ref. 38.

The first-order wave function $\psi_{\text{pol}}^{(100)}$ can be conveniently written as

$$\psi_{\text{pol}}^{(100)} = \psi_{\text{ind}}^{(1)(A - B) \Psi_0^B \Psi_0^C + \psi_{\text{disp}}^{(1)(B - A) \Psi_0^B \Psi_0^C + \psi_{\text{disp}}^{(1)(A - B) \Psi_0^C]},$$

where $\psi_{\text{ind}}^{(1)(X - Y) \Psi_0^X \Psi_0^Y}$ is the standard induction wave function corresponding to the polarization of the monomer $X$ by the monomer $Y$, and $\psi_{\text{disp}}^{(1)(X - Y) \Psi_0^X \Psi_0^Y}$ is the dispersion wave function for the pair $XY$. Equation (60) shows that the second-order exchange nonadditivity splits into the exchange-induction $[E_{\text{exch-ind}}(3,3)]$ and exchange-dispersion $[E_{\text{exch-disp}}(3,3)]$ three-body contributions. Obviously, the expressions for exchange-induction and exchange-dispersion components of $E_{\text{exch-ind}}^{(200)}(3,3)$ and $E_{\text{exch-disp}}^{(110)}(3,3)$ can be obtained by replacing in Eqs. (58) and (59) the polarization wave functions $\psi_{\text{pol}}^{(100)}$ and $\psi_{\text{pol}}^{(010)}$ by their induction or dispersion counterparts, i.e.,

$$E_{\text{exch-ind}}^{(200)}(3,3) = \langle \Psi_0 | (V^{AB} - \langle V^{AB} \rangle) (Q^{AB} - \langle Q^{AB} \rangle) \rangle \times \psi_{\text{ind}}^{(1)(A - B) \Psi_0^B \Psi_0^C} + \psi_{\text{disp}}^{(1)(B - A) \Psi_0^B \Psi_0^C},$$

and

$$E_{\text{exch-disp}}^{(110)}(3,3) = \langle \Psi_0 | (V^{BC} - \langle V^{BC} \rangle) (P - \langle P \rangle \rangle \psi_{\text{pol}}^{(100)} + \psi_{\text{disp}}^{(1)(C - B) \Psi_0^C},$$

respectively.
\[
\times (P - \langle P \rangle) [\Psi_{\text{ind}}^{(1)}(A \rightarrow B) \Psi^B_0 \Psi^C_0 + \Psi^A_{\text{ind}}(B \rightarrow A) \Psi^C_0].
\]

(62) \n
\[E_{\text{exch-disp}}^{(200)}(3,3) = (\langle \Psi_0 | (V^{AB} - \langle V^{AB} \rangle)(Q^{AB} - \langle Q^{AB} \rangle)\times \Psi_{\text{disp}}^{(1)}(A \cdots B) \Psi^C_0 \rangle,
\]

(63) \n
\[E_{\text{exch-disp}}^{(110)} = (\langle \Psi_0 | (V^{AB} - \langle V^{AB} \rangle)(P - \langle P \rangle) \Psi^A_{\text{disp}}(B \cdots C) + \langle \Psi_0 | (V^{BC} - \langle V^{BC} \rangle)(P - \langle P \rangle) \Psi^C_{\text{disp}}(A \cdots B) \rangle.
\]

(64) \n
Since the exchange-induction and exchange-dispersion energies are small even for pair interactions, and since calculations employing correlated wave functions are not feasible even in the two-body case, we will neglect the intramonomer correlation effects on these components. This can be achieved by replacing in Eqs. (61)–(64) the exact \( \Psi_0 \) by the product of Hartree–Fock determinants of the monomers, \( \Phi_0 = \Phi_0^A \Phi_0^B \Phi_0^C \), and the exact induction and dispersion wave functions by their counterparts neglecting the intramonomer correlation effects [denoted by \( \Phi^{(1)}_{\text{ind}}(X \rightarrow Y) \) and \( \Phi^{(1)}_{\text{disp}}(X \cdots Y) \), respectively]. It can be shown that the wave function

\[ \Phi^{(100)}_{\text{pol}} = \Phi^{(1)}_{\text{ind}}(A \rightarrow B) \Phi^B_0 \Phi^C_0 + \Phi^A_{\text{ind}}(B \rightarrow A) \Phi^C_0 + \Phi^{(1)}_{\text{disp}}(A \cdots B) \Phi^C_0. \]

(65)

can be written as

\[ \Phi^{(100)}_{\text{pol}} = [T^{(100)}_{110} + T^{(100)}_{010} + T^{(100)}_{110}] \Phi_0, \]

(66)

where the operators \( T^{(100)}_{110}, T^{(100)}_{010}, \) and \( T^{(100)}_{110} \) are defined explicitly as

\[ T^{(100)}_{110} = (t_B)^{\sigma} a^{\sigma}_B, \quad T^{(100)}_{010} = (t_A)^{\beta} b^{\beta}_A, \quad T^{(100)}_{110} = (t_{\beta A})^{\rho} \rho^{\alpha}_B b^{\beta}_A. \]

(67)

(See the beginning of Sec. II for the notation.) One can also show that

\[ T^{(100)}_{110} \Phi_0 = \Phi^{(1)}_{\text{ind}}(A \rightarrow B) \Phi_0^B \Phi^C_0, \]

(68)

\[ T^{(100)}_{010} \Phi_0 = \Phi^B_0 \Phi^{(1)}_{\text{ind}}(B \rightarrow A) \Phi_0^C, \]

(69)

Furthermore, since the wave function \( \Phi^{(100)}_{\text{pol}} \) is purely additive, the amplitudes \( (t_B)^{\sigma} \), \( (t_A)^{\beta} \), and \( t_{\beta A}^{\rho} \) are the same as in the two-body case, and are explicitly given by

\[ (t_B)^{\sigma} = (\omega_B)^{\sigma} \rho^{\alpha}_p, \quad (t_A)^{\beta} = (\omega_A)^{\beta} \rho^{\alpha}_p, \quad t_{\beta A}^{\rho} = \rho^{\alpha}_p (\omega_A)^{\beta}, \]

(70)

where \( \epsilon^{\epsilon_1 \cdots \epsilon_n} = \epsilon^{\epsilon_1} \cdots \epsilon^{\epsilon_n} - \epsilon^{\epsilon_1} \cdots \epsilon^{\epsilon_{n-1}} - \cdots - \epsilon^{\epsilon_1} \cdots \epsilon^{\epsilon_n} \), and \( \epsilon \) and \( \epsilon' \) denotes the orbital energy associated with the spin–orbital \( \phi_k \).

Below we will use the following identity:

\[ (V^{AB} - \langle V^{AB} \rangle \Phi_0) \Phi_0 = \hat{V}^{AB} \Phi_0, \]

(71)

where

\[ \hat{V}^{AB} = \hat{V}^{AB}_{110} + \hat{V}^{AB}_{010} + \hat{V}^{AB}_{110}, \]

(72)

A similar definition holds for \( \hat{V}^{BC} \). Using Eqs. (68) and (69), and the identity (71) one can rewrite the formulas for the Hartree–Fock exchange-induction and exchange-dispersion nonadditivities as commutator expressions,

\[ E_{\text{exch-ind}}^{(200)}(3,3) = \langle [Q^{AB}, \hat{V}^{AB}] \Phi_0 (T^{(100)}_{100} + T^{(100)}_{010}) \Phi_0 \rangle, \]

(74)

\[ E_{\text{exch-ind}}^{(110)} = \langle [P, \hat{V}^{AB}] \Phi_0 (T^{(100)}_{100} + T^{(100)}_{010}) \Phi_0 \rangle, \]

(75)

\[ E_{\text{exch-disp}}^{(200)}(3,3) = \langle [\hat{V}^{ABC}, \Phi_0] (Q^{AB}, T^{(100)}_{110}) \Phi_0 \rangle, \]

(76)

\[ E_{\text{exch-disp}}^{(110)} = \langle [P, \hat{V}^{ABC}] \Phi_0 (P, T^{(100)}_{110}) \Phi_0 \rangle, \]

(77)

Note that similar to the two-body case, one can consider the exchange-induction energy fully accounting for the coupled-Hartree–Fock-type response, i.e., for the perturbation induced modification of the Hartree–Fock potential. The corresponding exchange-induction energies will be denoted by

\[ E_{\text{exch-ind,resp}}^{(200)}(3,3) \]

and \( E_{\text{exch-ind,resp}}^{(110)} \). The commutator formulas for these components are given by Eqs. (74) and (75), respectively, provided that the amplitudes of the single-excitation operators \( T^{(100)}_{110} \), etc., are replaced by the corresponding coupled-Hartree–Fock amplitudes.

Using the Wick and contraction theorems for the second-quantized operators, and performing integrations over spin variables, Eqs. (74)–(77) can be rewritten in terms of molecular integrals and orbital energies. One may note that since the \( V^{AB} \) operators are exclusively expressed in terms of Coulomb integrals, and various exchange operators in terms of overlap integrals, Eqs. (74)–(77) give the second-order exchange nonadditivity in terms of Coulomb and overlap integrals only (no exchange or hybrid integrals appear in the final expressions). The orbital expressions corresponding to Eqs. (74)–(77) are reported in Appendix B.

**III. MULTIPOLe EXPANSION OF THE THREE-BODY POLARIZATION CONTRIBUTIONS THROUGH THE THIRD-ORDER OF PERTURBATION THEORY**

In this section we will give the asymptotic (large \( R \)) expressions for the three-body polarization contributions by introducing the multipole expansions for \( V^{AB}, V^{BC}, \) and \( V^{CD} \). The great advantage of the multipole expansion is that it yields an expression for the interaction energy in which only properties of the free monomers appear and, moreover, the geometry dependence of the interaction energy components is given explicitly in terms of simple functions. We shall use the spherical form of the multipole expansion since in contrast to the Cartesian formalism it gives the orientational dependence of the interaction energy components in a closed form. Since the spherical expressions found in the literature are not presented in terms of monomer properties, we report the spherical multipole-expanded formulas for all the three-body polarization components that were introduced in Sec. II B 1. We will show how the three-body contributions to the...
interaction energy can be written solely in terms of the following monomer properties: multipole moments, frequency-dependent polarizabilities, and hyperpolarizabilities. In the expressions derived in this section these monomer properties are expressed with respect to an arbitrary space-fixed frame, whereas they are usually calculated (or measured) with respect to a set of body-fixed inertial axes on the molecule. The angular momentum coupling used in all our formulas has the purpose to make the transformation from the monomer properties in their own body-fixed frames to the space-fixed frame as simple as possible. All properties on each monomer are coupled to spherical tensors of rank \( \Lambda \) which transform under the frame rotation by the use of irreducible Wigner rotation matrices \( \mathbf{D}^{(\Lambda)}(\alpha, \beta, \gamma) \).

The geometry dependence of the interaction energy components is described by functions depending on the spherical polar coordinates of the vectors \( \mathbf{R}_{\text{XY}} \) pointing from \( X \) to \( Y \). We designate the polar angles of \( \mathbf{R}_{\text{XY}} \) by \( \hat{R}_{\text{XY}} \) (which is a unit vector along \( \mathbf{R}_{\text{XY}} \)), and its length by \( R_{\text{XY}} \). The functions describing the geometry are obtained by Clebsch–Gordan coupling of irregular harmonics, defined by

\[
\mathcal{C}_m^j (R_{\text{XY}}) = R_{\text{XY}}^{-j-1} C_m^j (\hat{R}_{\text{XY}}),
\]

where \( C_m^j \) is a spherical harmonic in Racah normalization.\(^95\)

The multipole expansion of \( V^{XY} \) reads\(^59\)

\[
V^{XY} = \sum_{l_x, l_y = 0}^{\infty} (-1)^{l_x} \left( 2l_x + 2l_y + 1 \right) \frac{2l_x + 2l_y}{2l_x} \mathcal{C}_m^{l_x} \mathcal{C}_m^{l_y} (R_{\text{XY}}) Q^{l_x} Q^{l_y} (0),
\]

where the triple product is defined as

\[
\mathcal{C}_m^{l_x} \mathcal{C}_m^{l_y} (R_{\text{XY}}) = \sum_{m, m_x, m_y} \left( \frac{l_x + l_y}{m} \frac{l_x}{m_x} \frac{l_y}{m_y} \right) \mathcal{C}_m^{l_x} (R_{\text{XY}}) Q^{l_x} (m_x) Q^{l_y} (m_y),
\]

and the expression between round brackets is a 3j-symbol. The quantity \( Q^{l_x} \) is a multipole operator of \( X \), i.e., an irreducible spherical tensor operator with components defined by

\[
Q^{l_x} \equiv \sum_{p \in X} \frac{1}{Z_p} \mathbf{e}^{l_x} (\hat{r}_p),
\]

where the summation index \( p \) runs over all particles, both electrons and nuclei, of the molecule \( X \), and \( Z_p \) are the charges of those particles. We will designate a reducible frequency-dependent polarizability by \( \alpha^{(l_x)}_{\mu \nu} (\omega) \). This quantity is obtained from the linear polarization propagator of Eq. (33) by replacing \( \alpha^{(l_x)}_{\mu \nu} \) and \( \alpha^{(l_y)}_{\mu \nu} \) by \( \mathcal{C}_m^{l_x} \) and \( \mathcal{C}_m^{l_y} \), respectively, and multiplying by \( -1 \). The corresponding irreducible polarizability \( \alpha^{(l_x \Lambda \Lambda)}_{\mu \nu} (\omega) \) is obtained by Clebsch–Gordan coupling. In general the Clebsch–Gordan coupled product of spherical tensors will be denoted as \( [T \otimes S]_{M} \) i.e., as a binary product between square brackets,

\[
[T \otimes S]_{M} = \sum_{m, m'} \langle l, m; l', m' | L, M \rangle T_{m}^{l} S_{m'}^{l'},
\]

A. The multipole expansion of \( E^{\text{ind}}_{110} \)

After expanding \( V^{AB} \) and \( V^{BC} \) in the expression (42) of \( E^{\text{ind}}_{110} \), we find in the numerator

\[
\left[ \mathcal{C}_m^{l_x} (R_{AB}) \otimes (Q^{l_x}) \otimes (Q^{l_y})_{0n} \right]_0 \times \left[ \mathcal{C}_m^{l_y} (R_{BC}) \otimes (Q^{l_y})_{0n} \otimes (Q^{l_y})_{0n} \right]_0,
\]

where \( (Q^{l_y})_{0n} \) is the transition moment \( \langle \Psi_{\theta, \phi} | Q^{l_y} | \Psi_{\theta, \phi} \rangle \). In order to rewrite this expression, so that the static polarizability of \( \alpha_{\Lambda \Lambda}^{(l_y)} (\Lambda \Lambda) (0) \) appears, it is necessary to apply a recoupling procedure. It is not very difficult to show that

\[
2 \Re \sum_{n > 0} \left[ \mathcal{C}_m^{l_x} (R_{AB}) \otimes (Q^{l_x}) \otimes (Q^{l_y})_{0n} \right]_0 \times \left[ \mathcal{C}_m^{l_y} (R_{BC}) \otimes (Q^{l_y})_{0n} \otimes (Q^{l_y})_{0n} \right]_0 \times \left[ \eta_{M} \right]_{L}^{L} \eta_{M}^{L} (l_x l_y l_x'M),
\]

where \( \eta_{M}^{L} \) is the transition moment \( \langle \Psi_{\theta, \phi} | Q^{l_y} | \Psi_{\theta, \phi} \rangle \) obtained from the linear polarization propagator of Eq. (33) by replacing \( \alpha^{(l_x)}_{\mu \nu} \) and \( \alpha^{(l_y)}_{\mu \nu} \) by \( \mathcal{C}_m^{l_x} \) and \( \mathcal{C}_m^{l_y} \), respectively, and multiplying by \( -1 \). The corresponding irreducible polarizability \( \alpha^{(l_y \Lambda \Lambda)}_{\mu \nu} (\omega) \) is obtained by Clebsch–Gordan coupling. In general the Clebsch–Gordan coupled product of spherical tensors will be denoted as \( [T \otimes S]_{M} \) i.e., as a binary product between square brackets,

\[
[T \otimes S]_{M} = \sum_{m, m'} \langle l, m; l', m' | L, M \rangle T_{m}^{l} S_{m'}^{l'},
\]

B. The multipole expansion of \( E_{\text{pol}}^{(210)} \)

Before discussing the different physical effects such as induction–dispersion and induction, we first consider the angular momentum aspects of the multipole expansion and derive a generic expression for \( E_{\text{pol}}^{(210)} \) in terms of irreducible monomer tensors.

In the numerators of \( E_{\text{pol}}^{(210)} \) we meet products of the type

\[
\left[ \mathcal{C}_m^{l_x} (R_{AB}) \otimes (Q^{l_x}) \otimes (Q^{l_y})_{0n} \right]_0 \times \left[ \mathcal{C}_m^{l_y} (R_{BC}) \otimes (Q^{l_y})_{0n} \otimes (Q^{l_y})_{0n} \right]_0, \]
where the irreducible tensors \( T'_m \) are either transition matrix elements or expectation values of multipole operators \( Q'_m \).

The simplest angular dependence of the multipole expanded form of \( E_{\text{pol}}^{(210)} \) is obtained when we recouple these products such that the tensors belonging to one monomer are first coupled to an irreducible monomer tensor. Furthermore it is useful to apply the Gaunt series, which can be written as

\[
[\gamma^A \otimes \gamma^B \otimes \gamma^C]_{L_0} = G_{L_0} R^{l_l - l_l' - l_l''} 2 C^{l_l}_{l_l'}(\bar{R})
\]

with

\[
G_{L_0} = (-1)^{l_l - l_l'} [2L + 1]^{1/2} \begin{bmatrix} l_l' & l_l'' & L \\ 0 & 0 & 0 \end{bmatrix}.
\]

On system \( B \) we have tensors of order \( l_B, l_B' \), and \( l_B'' \). Below we will consider the coupling scheme \( \{l_B, l_B', l_B''\} \). However, sometimes a different scheme is called for. For instance, when \( l_B \) labels a permanent moment and \( l_B' \) and \( l_B'' \) label transition moments, it is better to couple first the latter two tensors, so that an irreducible polarizability is obtained. If such a case occurs, the monomer tensor may be recoupled, which yields an extra sum and 6j-symbols.

An alternative approach was followed by Piecuch,\(^{38}\) who considered in this case all 15 quantum numbers simultaneously and obtained 15j-symbols as recoupling coefficients.

We are then left with an arbitrary choice in the coupling order of the monomer tensors. We can, for example, couple first the tensors on \( A \) and \( C \), and then \( B \) (which is essentially the choice made by Piecuch), or first \( B \) and \( C \) and then \( A \). Since the second choice yields a recoupling constant that is a product of a 9j-symbol times two 6j-symbols, and the first choice gives a product of two 9j-symbols, we do not follow Piecuch, but take the second possibility. Recall in this connection that a 9j-symbol is a sum of ternary products of 6j-symbols.

We write

\[
[\gamma^A + l_B \otimes T^A \otimes T^B]_{L_0} \times \gamma^C \times \gamma^B \otimes \gamma^C]_{L_0} = G_{l_l + l_l' - l_l''} R^{l_l'' - l_l' - l_l'' - 2} 2 C^{l_l''}_{l_l'}(\bar{R})
\]

where the sum runs over the index set \( \{l\} = \{l_A, l_B, l_B', l_B'', l_C\} \) and \( Z_{\alpha\beta\gamma} \) is a recoupling coefficient, which is evaluated by means of Jacys diagrams in Fig. 1. Its value is

\[
(-1)^{l_A + l_B + l_C} \left[ \begin{array}{ccc} l_A & l_B & l_C \\ l_A & l_B & l_C \end{array} \right]_{L_{AB}}
\]

Finally, we obtain the generic term of the multipole expanded form of \( E_{\text{pol}}^{(210)} \),

\[
E_{\text{pol}}^{(210)} \rightarrow \sum_{\{l\}} \sum_{\{j\}} \sum_{M} \xi_{ij}^{(l)}[A_{\mu_A}^{A} \otimes B_{\mu_B}^{B} \otimes C_{\mu_C}^{C}]_{M}^{(lA_{\mu_A}^{A}, lB_{\mu_B}^{B}, lC_{\mu_C}^{C})}.
\]
Since different definitions of the (reducible) hyperpolarizability tensor can be found, we give its explicit definition, which agrees with our earlier definition, Eq. (36), of the quadratic polarization propagator.

\[ B_{\mu_B} = \sum_{\lambda_B} (-1)^{l_B + \lambda_B + \Lambda_B} \begin{pmatrix} l_B & \lambda_B & l'_B \\ \Lambda_B & \lambda'_B & l'_B \end{pmatrix} \times \left( \left( Q^{l_B} \otimes \alpha^{l_B} \right) \delta_B(0) \right)_{\mu_B} \]

\[ C_{\mu_C} = (Q^{L_C}) \]

where \( Q^l \equiv Q^l_m - \langle Q^l_m \rangle \). Two successive Clebsh–Gordan couplings give the irreducible monomer tensor \( R^{l_m}_{m'}(\omega_1, \omega_2) \). This tensor plays a role in the nonlinear optical process of two-wave mixing.

The multipole expansion gives an expression for \( E_{\text{pol}}^{(11)}(B \rightarrow A, C) \) [Eq. (49)] in the form of Eq. (85), if we substitute

\[ A_{\mu_A}^A = \frac{1}{2} \left( (Q^A) \otimes (Q^A) \right)_{\mu_A} \]

\[ B_{\mu_B}^A = \beta^{((l_B')_m m_{l_B'})}_{\mu_B} \delta_B(0,0), \]

\[ C_{\mu_C}^A = (Q^{L_C}) \]

We obtain the multipole expanded form of \( E_{\text{pol}}^{(11)} \) when we make the substitution into Eq. (85) of

\[ \left[ (A^A \otimes [B^A \otimes C^A]_{AB}) \right]_L \]

\[ = \frac{1}{4 \pi} \int_{-\infty}^{\infty} \left[ \alpha^{((l_A')_m m_{l_A'})} \Lambda_A(i \omega) \otimes \beta^{((l_B')_m m_{l_B'})} \Lambda_B(-i \omega, 0) \right] \otimes (Q^{L_C})_{\mu_C} d \omega. \]

Since the tensor on \( C \) is independent of \( \omega \), it is convenient to recouple the threefold irreducible product, by first coupling the tensors on \( A \) and \( B \), performing the Casimir–Polder integral over \( \omega \), and only then couple the permanent moment on \( C \) to the integral,

\[ \left[ (A^A \otimes [B^A \otimes C^A]_{AB}) \right]_L \]

\[ = \frac{1}{4 \pi} \sum_{M} \left( -1 \right)^{\lambda_A + \lambda_B + \lambda_{AB}} \times \left[ \Lambda_{M}, \Lambda_{AB} \right] \left( (Q^{L_C}) \right) \]

\[ = \left[ \left( T^A \otimes T^B \right) \right]_{[A^B]} \otimes \left( T^C \otimes T^D \right)_{[B^C]} \otimes \left( T^E \otimes T^F \right)_{[C^D]} \]

with the coupled angular function defined as follows (for typographical reasons a number of indices are suppressed):

\[ G_{M}^{L_{ij}}(R_{AB}, R_{BC}, R_{CA}) = \left[ \left( T^A \otimes T^B \right) \right]_{[A^B]} \otimes \left( T^C \otimes T^D \right)_{[B^C]} \otimes \left( T^E \otimes T^F \right)_{[C^D]} \]

\[ \times \sum_{M} \left( -1 \right)^{L + M} G_{M}^{L_{ij}}(R_{AB}, R_{BC}, R_{CA}) \cdot \mathcal{F}_{M}^{L_{ij}}. \]

The coupled (permanent or transition) moments \( T_{M}^{ij} \) are contained in the tensor \( \mathcal{F}_{M}^{L_{ij}} \), which is defined by

\[ \mathcal{F}_{M}^{L_{ij}} = \left[ \left( T^A \otimes T^B \right) \right]_{[A^B]} \otimes \left( T^C \otimes T^D \right)_{[B^C]} \otimes \left( T^E \otimes T^F \right)_{[C^D]} \]

\[ \otimes \left[ T^C \otimes T^D \right]_{[C^D]} \otimes \left( T^E \otimes T^F \right)_{[C^D]} \]

It is convenient to recouple \( \mathcal{F}_{M}^{L_{ij}} \) so that the moments on the same monomer are precoupled. The recoupling coefficient is proportional to a 15j-symbol of the fourth kind. We can write it out and obtain...
Then the generic term becomes

\[ E_{\text{pol}}^{(111)} \to \sum_{\{l'|l'\}M} \sum_{\{l''\}M} \left( -1 \right)^M \hat{\xi}^{(I')}_{II'} \Gamma^D_{JM} (R_{AB}, R_{BC}, R_{CA}) \times \left[ \left[ \{T^A \otimes T^C\}^J A^\alpha \otimes \left[ T^B \otimes T^B \right]^\beta \right]^A_{AB} \otimes \left[ T^C \otimes T^C \right]^C_{CM} \right] \]

The energy \( E_{\text{ind}}^{(111)} \) is one of the three terms of the induction energy \( E_{\text{ind}}^{(111)} \). We find its multipole expanded form by considering the appropriate sum over states and corresponding energy denominators, Eq. (51). The required formula can be obtained by substitution into Eq. (96) of

\[ \{T^A \otimes T^C\}^J A^\alpha = \alpha_{\mu A}^{(I')}, \]

\[ \{T^B \otimes T^B\}^\beta = \beta_{\mu B}^{(I')}, \]

\[ \{T^C \otimes T^C\}^C_{CM} = \alpha_{\mu C}^{(I')}. \]

The coupled permanent moments of \( A \) and \( C \) appear in the other two induction terms, which we do not give explicitly.

The Axilrod–Teller–Muto \( J^2 \) energy \( E_{\text{disp}}^{(111)} \), generalized to arbitrary multipoles, is obtained when we substitute into Eq. (96)

\[ \left[ \left[ \{T^A \otimes T^C\}^J A^\alpha \otimes \left[ T^B \otimes T^B\right]^\beta \right]^A_{AB} \otimes \left[ T^C \otimes T^C\right]^C_{CM} \right] \]

\[ = \frac{1}{2\pi} \int_0^{\infty} \left[ \left[ \alpha_{\mu A}^{(I') \lambda A} (-i\omega) \otimes \alpha_{\mu B}^{(I' B) \lambda B} (i\omega) \right]^A_{AB} \right. \]

\[ \otimes \alpha_{\mu C}^{(I' C) \lambda C} (i\omega), \]

\[ \left( \right)_{CM} d\omega. \]

**IV. SUMMARY**

In this paper we have developed the symmetry-adapted perturbation theory for a direct calculation of pairwise nonadditive polarization and exchange contributions to the interaction potentials of closed-shell trimers. We have shown that the three-body polarization contributions through the third order of perturbation theory naturally separate into terms describing the pure induction, mixed induction-dispersion, and pure dispersion interactions. Each term has a clear, partly classical, partly quantum mechanical, physical interpretation. Working equations for these components in terms of molecular integrals and linear and quadratic response functions have been derived. Assuming some approximations to the response functions, these formulas can be used in actual calculations. In the present paper we reported explicit orbital formulas for the second- and third-order three-body polarization contributions in the random-phase approximation. Also, the asymptotic expressions for the second- and third-order three-body polarization contributions in terms of the multipole moments and (hyper)polarizabilities of the isolated monomers have been derived.

We have also shown how the exchange terms can be classified, and derived explicitly connected commutator expressions involving second-quantized operators, as well as explicit orbital expressions, for the simplest approximations (neglecting intramonomer correlation effects). In the subse-
quent paper we present some illustrative applications of this theory to a system of current experimental interest, \( \text{Ar}_2 \cdot \text{HF}. \)

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**APPENDIX A: ORBITAL FORMULAS FOR THE POLARIZATION CONTRIBUTIONS IN THE RANDOM PHASE APPROXIMATION**

To derive orbital formulas for the three-body polarization contributions in the RPA approximation we need explicit orbital equations for the RPA linear and quadratic response functions. The polarization propagator, Eq. (33), can be expressed in the RPA approximation by the following spectral expansion:

\[
\Pi_{\kappa \kappa'}^{\lambda\lambda'}(\omega) = \sum_{n \neq 0} \left\langle \Phi_{\kappa}^{\lambda}\left|a_{\kappa}^{\lambda},O_{\kappa}^{\lambda}\right.\Phi_{\kappa'}^{\lambda'}\right\rangle \frac{\left(\Phi_{\kappa}^{\lambda}\right)\left(a_{\kappa}^{\lambda},O_{\kappa}^{\lambda}\right)\left(\Phi_{\kappa'}^{\lambda'}\right)}{\omega_n^2 - \omega + i\epsilon}.
\]

The RPA amplitudes \( \left(\Phi_{\kappa}^{\lambda}\right)_{\alpha}^{\beta} \) and \( \left(Y_{\kappa}^{\lambda}\right)_{\alpha}^{\beta} \), and the RPA excitation energies \( \omega_n^2 \) are solutions of the generalized eigenvalue problem,

\[
(\epsilon_{\alpha} - \epsilon_{\alpha})(X_{\kappa}^{\lambda})_{\alpha}^{\beta} + w_{\alpha\beta}(X_{\kappa}^{\lambda})_{\alpha}^{\beta} + w_{\alpha\beta}(Y_{\kappa}^{\lambda})_{\alpha}^{\beta} = \omega_n^2(X_{\kappa}^{\lambda})_{\alpha}^{\beta},
\]

(\( \epsilon_{\alpha} - \epsilon_{\alpha} \))\( (Y_{\kappa}^{\lambda})_{\alpha}^{\beta} + w_{\alpha\beta}(Y_{\kappa}^{\lambda})_{\alpha}^{\beta} + w_{\alpha\beta}(Y_{\kappa}^{\lambda})_{\alpha}^{\beta} = -\omega_n^2(Y_{\kappa}^{\lambda})_{\alpha}^{\beta}, \)

where \( w_{\alpha\beta} = w_{\lambda\lambda'}^{\kappa\kappa'} - w_{\kappa\kappa'}^{\lambda\lambda'} \). The solutions of Eq. (A3) are subject to the following normalization conditions:

\[
(X_{\kappa}^{\lambda})_{\alpha}^{\beta} - (Y_{\kappa}^{\lambda})_{\alpha}^{\beta} = \delta_{n\kappa},
\]

where \( (X_{\kappa}^{\lambda})_{\alpha}^{\beta} = [\langle X_{\kappa}^{\lambda}\rangle_{\alpha}^{\beta}]^\ast \), and a similar relation holds for \( (Y_{\kappa}^{\lambda})_{\alpha}^{\beta} \). The expression for the quadratic response function is somewhat more involved, and it can be deduced from Eq. (57) of Ref. 99.

Using the Wick theorem one can derive the following equivalent of Eq. (A1):

\[
\Pi_{\kappa \kappa'}^{\lambda\lambda'}(\omega) = \sum_{n \neq 0} \left\langle \Phi_{\kappa}^{\lambda}\left|a_{\kappa}^{\lambda},O_{\kappa}^{\lambda}\right.\Phi_{\kappa'}^{\lambda'}\right\rangle \frac{\left(\Phi_{\kappa}^{\lambda}\right)\left(a_{\kappa}^{\lambda},O_{\kappa}^{\lambda}\right)\left(\Phi_{\kappa'}^{\lambda'}\right)}{\omega_n^2 - \omega + i\epsilon}.
\]

Substituting Eq. (A5) and a similar equation for \( \Pi_{\kappa \kappa'}^{\lambda\lambda'}(\omega_1, \omega_2) \) into Eqs. (44), (46), (48), (50), (52), and (54) and performing integrations over spin coordinates one gets the explicit orbital formulas for the polarization contributions in the RPA approximation. An important simplification occurs if one assumes that the orbitals are real. It turns out that all polarization contributions can be written in terms of one spin-free combination of the RPA amplitudes,

\[
(V_{n})_{\alpha}^{\beta} = \frac{1}{2} \left[ (X_{n})_{\alpha}^{\beta} + (Y_{n})_{\alpha}^{\beta} \right] + (Y_{n})_{\alpha}^{\beta} + (Y_{n})_{\alpha}^{\beta} + (Y_{n})_{\alpha}^{\beta}, \quad \text{(A6)}
\]

where the indices \( k^+ \) and \( k^- \) refer to spin orbitals obtained by multiplication of the spatial orbital \( \psi_k \) by the spin functions \( \alpha \) and \( \beta \), respectively. The spin-free amplitudes of Eq. (A6) fulfill an eigenvalue problem similar to Eq. (A3).

[Note that the spin-free amplitudes of Eq. (A6) correspond to the \( D \) amplitudes given by Eq. (14) of Ref. 89.] Furthermore, since in some expressions only static RPA propagators appear, it is useful to introduce coupled-Hartree–Fock (CHF) coefficients defined as

\[
(C_B)_{\alpha}^{\beta} = -2 \sum_{n > 0} (V_n)_{\alpha}^{\beta} (\omega_B)_{\alpha}^{\beta} (V_n)_{\alpha}^{\beta} / \omega_n^2.
\]

Similar definitions hold for \( (C_A)_{\alpha}^{\beta} \), etc. Thus, assuming that the orbitals are real, the orbital forms of Eqs. (44) and (46)–(54) are given by

\[
\text{Eq}(3.3) = 4(C_B)_{\alpha}^{\beta} (\omega_B)_{\alpha}^{\beta} + 4(C_C)_{\alpha}^{\beta} (\omega_C)_{\alpha}^{\beta} + 4(C_A)_{\alpha}^{\beta} (\omega_A)_{\alpha}^{\beta} + 4(C_A)_{\alpha}^{\beta} (\omega_B)_{\alpha}^{\beta}.
\]

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\[ E^{(3)}_{\text{disp}}(3,3) = 128 \sum_{n,m,p \neq 0} u_{ab}^r v_{bi}^r v_{ci}^r \frac{1}{(\omega_n^A + \omega_m^B)(\omega_n^C + \omega_p^C)} + \frac{1}{(\omega_n^A + \omega_m^B)(\omega_m^B + \omega_p^C)} \]

\[ \left[ (V_n^r)^a v_{ab}^r (V_m^r)_b^c (V_p)_c^d \left( \sum_{i=1}^{n,m,p} \frac{1}{\omega_n^A + \omega_m^B}(\omega_n^A + \omega_p^C) \right) \right] \]

\[ E^{(210)}_{\text{ind-disp}} = 32 \sum_{n,m \neq 0} \frac{(V_n)_d^a v_{ab}^r (V_m)_b^c (V_p)_c^d}{\omega_n^A + \omega_m^B} \]

\[ + 32 \sum_{n,m \neq 0} \frac{(V_n)^a v_{ab}^r (V_m)^b (V_p)_c^d}{(\omega_n^A + \omega_m^B)(\omega_n^A + \omega_m^B)} \]

\[ + 64 \sum_{n,m \neq 0} \frac{(V_n)^a v_{ab}^r (V_m)_b^c (V_p)_c^d}{(\omega_n^A + \omega_m^B)(\omega_m^B + \omega_p^C)} \]

\[ + 128 \sum_{n,m \neq 0} \frac{(V_n)_d^a v_{ab}^r (V_m)_b^c (V_p)_c^d}{\omega_n^A + \omega_m^B} \]

**APPENDIX B: ORBITAL FORMULAS FOR THE EXCHANGE CONTRIBUTIONS**

The orbital formulas for the second-order exchange contributions, Eqs. (74)-(77), can be obtained by a straightforward application of the Wick theorem, followed by the integration over spin variables, and are given by

\[ E^{(200)}_{\text{exch-ind}}(3,3) = 2(\omega_B)_b^a (t_A)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) - 2(\omega_B)_a^b (t_B)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) \]

\[ + 2(\omega_B)_a^b (t_A)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) - 2(\omega_B)_b^a (t_B)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) \]

\[ + 2(\omega_B)_b^a (t_A)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) + 2(\omega_B)_a^b (t_B)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) \]

\[ + 2(\omega_B)_a^b (t_A)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) + 2(\omega_B)_b^a (t_B)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) \]

\[ + 4(\omega_B)_a^b (t_A)_c^d (-S^c S^d + S^c S^d + S^c S^d + S^c S^d) \]

\[ E^{(110)}_{\text{exch-ind}} = 16 (\omega_B)_b^a (t_A)_c^d \]

\[ E^{(210)}_{\text{exch-ind}} = 16 (\omega_B)_a^b (t_A)_c^d \]

where $\delta_{kk'} = 2\delta_{kk'} - \delta_{kk'}$, and the intermediate quantity $\left( W_{n,m} \right)_b$ is defined as

\[ (W_{n,m})_b = \frac{(V_n)^a (V_m)_b^c (V_p)_c^d}{\omega_n^A + \omega_m^B} (m \rightarrow m') \]

\[ \left( W_{n,m} \right)_b = (V_n)^a (V_m)_b^c (V_p)_c^d (m \rightarrow m') \]

\[ \left( W_{n,m} \right)_b = (V_n)^a (V_m)_b^c (V_p)_c^d (m \rightarrow m') \]

\[ \left( W_{n,m} \right)_b = (V_n)^a (V_m)_b^c (V_p)_c^d (m \rightarrow m') \]
\[ + S_{ab}^{c} S_{ab}^{b} + 2(\omega_{C})_{C}^{rb}(-S_{ab}^{c} S_{ab}^{b}) + 2(\omega_{B})_{B}^{rb}(-S_{ab}^{c} S_{ab}^{b}) + 2(\omega_{C})_{C}^{rb}(-S_{ab}^{c} S_{ab}^{b}) + 2(\omega_{B})_{B}^{rb}(-S_{ab}^{c} S_{ab}^{b}) \]

(B2)

\[ E_{\text{exch-disp}}^{(200)}(3,3) = 2(\omega_{B})_{B}^{rb}(-S_{ab}^{c} S_{ab}^{b}) + 2(\omega_{C})_{C}^{rb}(-S_{ab}^{c} S_{ab}^{b}) - 4(\omega_{B})_{B}^{rb} S_{ab}^{c} S_{ab}^{b} - 4(\omega_{C})_{C}^{rb} S_{ab}^{c} S_{ab}^{b} \]

(B3)

\[ E_{\text{exch-disp}}^{(110)} = 2(\omega_{B})_{B}^{rb}(-S_{ab}^{c} S_{ab}^{b}) + 2(\omega_{C})_{C}^{rb}(-S_{ab}^{c} S_{ab}^{b}) - 4(\omega_{B})_{B}^{rb} S_{ab}^{c} S_{ab}^{b} - 4(\omega_{C})_{C}^{rb} S_{ab}^{c} S_{ab}^{b} \]

(B4)


