Physical mechanisms of intermolecular interactions from symmetry-adapted perturbation theory

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Abstract

Symmetry-adapted perturbation theory (SAPT) is a method for computational studies of noncovalent interactions between molecules. This method will be discussed here from the perspective of establishing the paradigm for understanding mechanisms of intermolecular interactions. SAPT interaction energies are obtained as sums of several contributions. Each contribution possesses a clear physical interpretation as it results from some specific physical process. It also exhibits a specific dependence on the intermolecular distance. The four major contributions are the electrostatic, induction, dispersion, and exchange energies, each due to a different mechanism, valid at any intermolecular separation R. In addition, at large R, SAPT interaction energies are seamlessly connected with the corresponding terms in the asymptotic multipole expansion of interaction energy in inverse powers of R. Since such expansion explicitly depends on monomers' multipole moments and polarizabilities, this connection provides additional insights by rigorously relating interaction energies to monomers' properties.

Keywords: intermolecular interactions; non-covalent interactions; symmetry-adapted perturbation theory; physical components of interaction energy.

I. INTRODUCTION

Weak or noncovalent interactions (NCIs) between molecules are responsible for physical properties of gases, liquids, molecular crystals, biomolecular aggregates, and soft condensed matter. Thus, such interactions are of utmost importance for all matter that surrounds us, including living organisms. For these reasons, Richard Feynman in his "Lectures on Physics" stated that "If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the *atomic hypothesis* (or the atomic fact, or whatever you wish to call it) that *all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another*" [although Feynman talks about atoms, a picture under this sentence shows an ensemble of water molecules]. NCIs are at least an order of magnitude weaker than the chemical (covalent) interactions that bind atoms in molecules. This ratio of strengths makes it natural to study intermolecular interactions using perturbation theory. Such approach is generally known as symmetry-adapted perturbation theory (SAPT). The basic assumption of SAPT is the partitioning of the total Hamiltonian H of interacting molecules into the sum of the Hamiltonians of separated monomers, $H_0 = H_A + H_B + \dots$, and of the perturbation operator V that collects Coulomb interactions of the electrons and nuclei of a given monomer with those of the other monomers: $V = V_{AB} + V_{AC} + V_{BC} + \dots$. The solution of the zeroth-order problem, i.e., of the Schrödinger equation $H_0\Phi_0 = E_0\Phi_0$, is then the product of the wave functions of free, noninteracting monomers. Such product is not fully antisymmetric since permutations of electrons between different monomers do not result only in a change of the sign of the wave function. Thus, such product has to be properly antisymmetrized to satisfy Pauli's exclusion principle, and this is the origin of the phrase "symmetry-adapted". For large intermonomer separations R, one can omit the antisymmetrization and use the Rayleigh-Schrödinger perturbation theory (RSPT), the simplest form of intermolecular perturbation theory. This approach applied to intermolecular interactions was termed by Hirschfelder[1] the "polarization approximation". This name has been less used recently since it leads to confusions with the term "polarization" applied often to the induction interactions. Unfortunately, RSPT leads to unphysical behavior of the interaction energy at short R as it fails to predict the existence of the repulsive walls on the potential energy surfaces. This failure is the result of lack of the correct symmetry of the wave function under the exchanges of electrons between interacting monomers. Thus, to describe interactions everywhere in the intermonomer configuration space, one has to perform symmetry adaptation. There are several ways to do it, the simplest one is to (anti)symmetrize the wave functions of the RSPT method, leading to the symmetrized Rayleigh-Schrödinger (SRS) approach[2]. Significant research effort has been devoted to symmetry adaptations[1–18], however, only the SRS method is used in practice. Thus, from this point of view, present-day SAPT is unique. When SAPT is applied to many-electron systems, monomers can be described at various levels of electronic structure theory: from the Hartree-Fock (HF) level to the full configuration interaction (FCI) level. This leads to a hierarchy of SAPT levels of approximations depending on treatment of intramonomer electron correlation. However, in terms of expansion in powers of the intermolecular perturbation operator V, it is always the same SRS method, only each perturbation energy contribution $E^{(i)}$, where i is the order in V, is calculated more and more accurately as the description of monomers improves. Thus, there is only one flavor of SAPT used in practice (SRS) and differences between various implementations result from the assumed treatment of intramonomer correlation. The most relevant original papers on the developments of SAPT are Refs. 2, 18–33. Important developments in computer implementations are presented in Refs. 34–42. Several approximate versions of SAPT have been developed[43–52]. Most comprehensive reviews are Refs. 53–59. Basic ideas of SAPT are also presented in several textbooks[60–64].

An alternative way to compute interaction energies is the supermolecular method that consists in subtraction of the sum of the total monomer energies from the total energy of the interacting system. Both involved quantities are several orders of magnitude larger in magnitude than the result of this subtraction, i.e., the interaction energy. More importantly, the errors of the total energies are almost always larger than the magnitude of the interaction energy (except for few-electron systems treated using the most accurate electronic structure methods). Thus, the accuracy of the supermolecular approach depends to a large extent on error cancellations. Such cancellation actually does take place in many cases and the supermolecular approach can provide reliable approximations of interaction energies. In particular, the so-called basis set superposition errors (BSSE) can be removed using the counterpoise method[65]. In fact, SAPT provided a numerical proof that such cancellation does take place[66]. The removal of BSSE is more complicated in the methods that use explicitly-correlated basis sets[67,68].

The interaction energy obtained from the supermolecular approach is just a single number. Therefore, a large number of methods, called the energy decomposition analysis (EDA) methods[69–77], have been developed to partition this interaction energy into physical components. Such decomposition is nonunique and components designed to represent the same physical effects differ, often very significantly, when obtained using different EDA methods. In contrast, no decomposition of the total interaction energies is taking place in SAPT. Instead, interaction energies are assembled from uniquely defined contributions. Each contribution is rigorously defined by a basis-set-independent differential equation, so these contributions are well-defined in the infinite basis set limit (which is not the case for many EDA methods).

There are four major SAPT contributions: electrostatic, induction, dispersion, and exchange energies. While the first three are often viewed in terms of their asymptotic expansions, each of them has a clear physical interpretation at any R. The electrostatic part of the first-order SAPT energy, $E^{(1)}_{\rm elst}$, is the Coulomb interaction between unperturbed charge densities of monomers. The induction part of the second-order energy, $E^{(2)}_{\rm ind}$, is the effect of the modification of the electronic wave function of one monomer by the electric field of the unperturbed charge distribution of the interacting partner. The resulting change in the electronic density interacts then with the electric field of the unperturbed charge distribution of the interacting partner (however, there is a prefactor multiplying the Coulomb interaction of these densities, see Sec. III B). For clusters larger than dimers, the second-order induction interaction contributes to three-body energies since the perturbation of the density of monomer B due to monomer A interacts also with the unperturbed fields of the remaining monomers. The dispersion part of the second-order energy, $E^{(2)}_{\rm disp}$, is a quantum effect with no classical analog and results from correlations of positions of electrons of a given monomer with those of the electrons of the other monomers. The exchange energy (called also the exchange-repulsion energy) results from quantum tunneling of electrons between interacting monomers. This energy decays exponentially and, at small R, provides the repulsive wall on potential energy surfaces. See Sec. III for rigorous explanations of the physical mechanisms mentioned above.

The long-range SAPT components, i.e., those decaying at large R as inverse powers of R, can be accurately represented at large R by the multipole series (the sum of these series provides the asymptotic expansion of the total interaction energy[78]). Thus, there is a seamless connection between SAPT and the multipole series. This relation allows one to interpret SAPT components as resulting from interactions of monomers' multipole moments and multipole polarizabilities (including the dynamic polarizabilities appearing in the case of the dispersion interaction). At intermediate and small R, when the wave functions of monomers overlap in a significant way, the asymptotic expansion is not valid. Nevertheless, the multipole-based interpretation can still be used. The additional contributions that arise, referred to as the charge-overlap (or charge-penetration) effects, can be efficiently represented by damping factors multiplying individual terms in the multipole expansion[53,79–82]. Since approximate damping factors such as that proposed by Tang and Toennies[83] have values in the range (0,1), they always decrease the magnitude of a given multipole expansion component. As the result, damped expansions of induction and dispersion energies are above the (truncated) undamped ones. One may add that there exist contributions to the RSPT interaction energies that are not proportional to the components of the multipole expansion. These contributions decay exponentially[81], can be negative, and can be as large in magnitude as the damping contributions resulting from typical approximate damping factors. Due to these effects, the values of the unexpanded induction energy can lie significantly below the undamped multipole expansion values[84]. The asymptotic expansion is discussed in Sec. III E.

The focus of the present paper will be on SAPT contributions and their physical interpretation. SAPT is *the* theory of intermolecular forces. Chapters in textbooks devoted to intermolecular interactions use SAPT concepts even when they do not mention SAPT. As stated above: (a) SAPT contributions are defined in a rigorous way and can be calculated at complete basis set limits, i.e., exact values of each contribution can be potentially determined; (b) except for intermolecular distances much shorter than the van der Waals minimum distance, $R \ll R_{\rm vdW}$, where monomers lose their identity in the dimer, the sum of low-order SAPT contributions provides a very good approximation to the total interaction energy; (c) each contribution has a unique physical interpretation. Thus, SAPT can be viewed as constituting the "reference model" for EDA methods in the sense that the terms in an EDA decomposition corresponding to a given physical mechanism should be as close as possible to SAPT contributions representing the same physical effects. Some versions of EDA do define interaction energy contributions that do not appear in SAPT. The sum of such contributions is expected to be near zero since SAPT's low-order contributions sum up to an accurate value of the interaction energy, so no extra terms can be added. Alternatively, such contributions might be identified as parts of SAPT's contributions to interaction energies. Since EDA contributions by definition add up to the supermolecular interaction energy of the methods used in a given EDA, if an EDAs includes terms labeled in the same way as SAPT contributions plus some large non-SAPT basis-set dependent contributions, it means that the former are incompatible with the asymptotic expansion of the interaction energy (since SAPT is always compatible).

Two additional important aspects of SAPT should be mentioned here. One is that in practical terms, the accuracy of high-level versions of SAPT is similar to that of the coupled cluster method with single, double, and noniterative triple excitations [CCSD(T)] (see the discussion in Ref. 59). Another one is that since SAPT is a perturbation theory, SAPT interaction energies are computed directly, i.e., no subtractions of the total dimer and monomer energies, such as those performed in supermolecular approaches, are involved. Thus, there is no loss of accuracy resulting from subtractions of large numbers. In consequence, SAPT is free of BSSE, while BSSE may lead to artifacts in EDA results[85,86].

II. LEVELS OF INTRMONOMER ELECTRON CORRELATION IN SAPT

SAPT is formally an exact theory provided that computations are carried out to a high-order in V and exact monomer wave functions are used. This has been demonstrated by performing high-order RSPT/SAPT calculations for small dimers, such as for example Li–H or He–He, and comparing with FCI results[15,16,18,66,87–89] (see Refs. 54 and 59 for reviews of this work). To get high accuracy for many-electron systems, monomers have to be described at a correlated level, e.g., using many-body perturbation theory (MBPT) or CC methods. It turned out that if monomers are described by density-functional theory (DFT), such SAPT results are also comparable to the CCSD(T) ones in terms of accuracy, but are significantly less expensive to obtain.

SAPT approach can be applied to a cluster consisting of any number of monomers, but it has been implemented so far for two-body and three-body systems, i.e., dimers and trimers (however, the many-body expansion converges quickly, so this level is sufficient to describe large clusters and condensed phases[90–93]). In this paper, only two-body SAPT will be discussed from now on. For the three-body pairwise nonadditive contributions, see Refs. 23, 28, 90, 94, and 95. In two-body SAPT, the interaction energy is expanded as the series in powers of V:

$$E_{\rm int}^{\rm SAPT} = E_{\rm elst}^{(1)} + E_{\rm exch}^{(1)} + E_{\rm ind}^{(2)} + E_{\rm exch-ind}^{(2)} + E_{\rm disp}^{(2)} + E_{\rm exch-disp}^{(2)} + \ldots \tag{1}$$

where the subscripts indicate the physical contributions mentioned earlier. In particular, the corrections $E_{\rm exch-ind}^{(2)}$ ($E_{\rm exch-disp}^{(2)}$) result from antisymmetrization of the induction (dispersion) wave functions. Exact calculations of each term in Eq. (1) would require the knowledge of exact wave functions for the ground and excited states of each monomer. Such functions are, of course, generally unknown for larger monomers. The simplest approximate but realistic description of monomers is provided by the HF wave functions, which can be accurately computed even for very large monomers. With the HF description of monomers, the interaction energy through the second order in V can still be computed in several ways. The simplest approach is to use the following set of components

$$E_{\rm int}^{\rm SAPT(HF)}[2] = E_{\rm elst}^{(10)} + E_{\rm exch}^{(10)} + E_{\rm ind}^{(20)} + E_{\rm exch-ind}^{(20)} + E_{\rm disp}^{(20)} + E_{\rm exch-disp}^{(20)}, \tag{2}$$

where the second superscript indicates the HF level of theory and the uncoupled HF (UCHF) approach is applied in second order. The most advanced HF-level approach is to use in second order the coupled HF (CHF) static and dynamic density-density response functions, also referred to as frequency-dependent density susceptibilities (FDDSs), i.e., to compute the terms

$$\begin{aligned} E_{\rm int}^{\rm SAPT(CHF)}[2] = E_{\rm elst}^{(10)} + E_{\rm exch}^{(10)} + E_{\rm ind}^{(2)}({\rm CHF}) + E_{\rm exch-ind}^{(2)}({\rm CHF}) \\ + E_{\rm disp}^{(2)}({\rm CHF}) + E_{\rm exch-disp}^{(2)}({\rm CHF}). \end{aligned} \tag{3}$$

The name CHF originates from the method of computing polarizabilities, but this approach applied to frequency-dependent FDDSs is usually called the time-dependent HF (TD-HF)[96]. The CHF polarizabilities are known to be generally more accurate than the uncoupled ones obtained when the orbital response is neglected. The component $E_{\rm disp}^{(2)}$(CHF) can also be derived[97] using the random-phase approximation (RPA)[98], so it is sometimes denoted as $E_{\rm disp}^{(2)}$(RPA). The terms $E_{\rm ind/exch-ind}^{(2)}$(CHF) are usually denoted as $E_{\rm ind/exch-ind,resp}^{(20)}$ since the use of the static CHF density-density response functions is equivalent to the use of the induction wave functions computed accounting for the response of monomers' orbitals (thus the subscript "resp") and, consequently, of monomers' Fock operators to the electrostatic field of the interacting partner. The SAPT(HF) and SAPT(CHF) approaches are the same in first order. Note that the second-order terms in Eq. (2) can be written in terms of the UCHF density-density response functions, and that SAPT(HF) can also be called SAPT(UCHF). Equations (2) and (3) are actually rarely used. The reason is that while the corrections $E^{(2)}_{\mathrm{disp/exch-disp}}(\mathrm{CHF})$ are significantly more expensive to compute than the corrections $E^{(20)}_{\mathrm{disp/exch-disp}}$, the calculations of the two types of the corrections are of about the same costs in the case of induction and exchange-induction energies. Therefore, the most often used variant, denoted as SAPT0, is

$$E^{\mathrm{SAPT0}}_{\mathrm{int}} = E^{(10)}_{\mathrm{elst}} + E^{(10)}_{\mathrm{exch}} + E^{(20)}_{\mathrm{ind,resp}} + E^{(20)}_{\mathrm{exch-ind,resp}} + E^{(20)}_{\mathrm{disp}} + E^{(20)}_{\mathrm{exch-disp}}. \tag{4}$$

SAPT0 is a low- or at the best a moderate-accuracy approximation. The simplest way to improve it is to expand monomers' wave functions in powers of the intramonomer correlation operator $W = W_A + W_B$, where W_X is the Møller-Plesset (MP) fluctuation potential defined as the difference between monomer's Hamiltonian H_X and the sum of monomer's one-electron Fock operators. This leads to the wave-function based SAPT[21–23,55,58,97,99], with each contribution in Eq. (1) represented as

$$E^{(i)} = \sum_{j=0}^{n} E^{(ij)}, \tag{5}$$

where j denotes the order in W. In view of the reliance on the MP partitioning of monomer's Hamiltonians, the levels of SAPT based on Eq. (5) can be referred to as SAPT(MPn). Using the ideas of the coupled-cluster approach, one can perform selective infinite-order summations in W (Refs. 97, 99–105). The highest programmed level of the wave-function based SAPT corresponds to monomers described at the CCSD level and is denoted as the SAPT(CCSD) method[104,105]. Comparisons of SAPT and supermolecular MBPT/CC formulas for individual components[94,106] show that the highest programmed level of SAPT is approximately equivalent to the supermolecular CCSD(T) level. This is the case despite the fact that this level of SAPT does not include triple excitations in the description of monomers. However, mixed intra-/inter-monomer triple excitations are included. Agreement between high-level SAPT and supermolecular CCSD(T) indicates that intramonomer triple excitations make small contributions to interaction energies. In powers of V, the highest-level terms that have been developed are of the third-order[30,107,108]. With the highest available levels of intramonomer correlation, the wave-function based third-order SAPT is a very accurate method, but is not significantly less expensive than similarly accurate supermolecular MBPT/CC approaches.

SAPT based on the HF description of monomers is a low-cost method, but its errors can be as large as 30% (still, SAPT0 is considerably more accurate than the supermolecular HF approach since it accounts for the dispersion interactions). In contrast, SAPT based on the DFT description of monomers, SAPT(DFT), developed in Refs. 24–27,109–114, is about as expensive as SAPT(CHF), while SAPT(DFT) interaction energies are close in accuracy to those from CCSD(T) or from the high-level wave-function based SAPT (see Refs. 42, 59, and 115). In SAPT(DFT), the intramonomer correlation effects in interaction energies originate from the DFT-level representation of monomers, i.e., there is no expansion in powers of an operator analogous to W. Therefore, the second index in $E^{(ij)}$ is dropped and the counterpart of the expansion of Eq. (3) takes the form:

$$\begin{aligned} E_{\text{int}}^{\text{SAPT(DFT)}}[2] = E_{\text{elst}}^{(1)}(\text{KS}) + E_{\text{exch}}^{(1)}(\text{KS}) + E_{\text{ind}}^{(2)}(\text{CKS}) + E_{\text{exch-ind}}^{(2)}(\text{CKS}) \\ + E_{\text{disp}}^{(2)}(\text{CKS}) + E_{\text{exch-disp}}^{(2)}(\text{CKS}), \end{aligned} \tag{6}$$

where KS means that a given term is computed from asymptotically corrected[116,117] Kohn-Sham (KS) orbitals and orbital energies, while CKS stands for coupled KS and denotes components dependent on the coupled static or dynamic density-density response functions. These functions are computed using the time-dependent DFT (TD-DFT) method. It is important to realize that SAPT(DFT) interaction energies are dramatically more accurate than those resulting from a conventional supermolecular DFT calculation. In fact, for the majority of dimers, there is no resemblance between SAPT(DFT) and supermolecular DFT interaction energies: the former interaction energies are always very accurate, while the latter ones in many cases can be even of wrong sign (this happens in cases when the interaction energy is dominated by the dispersion energy, see Fig. 1 in Ref. 118).

There exists a simplified version of SAPT(DFT), referred to as SAPT(KS), in which the induction and dispersion corrections (including their exchange counterparts) are computed with the uncoupled KS response functions[109,113]. This SAPT(KS) method is algorithmically identical to the SAPT(HF) method and differs from the latter by replacing in the SAPT(HF) expressions the HF orbitals and orbital energies by the KS ones. Thus, SAPT(KS) calculations are of the same cost as SAPT(HF) ones, but are also of comparable accuracy (provided that KS calculations for monomers are asymptotically corrected). It turns out the use of the CKS response functions in SAPT(DFT) is critical for getting high accuracy. In contrast, the CHF dispersion energies are only moderately better than the UCHF ones[119] (i.e., than the corrections $E^{(20)}_{\mathrm{disp}}$). The reason is that the CHF dispersion energies, even if calculated with arbitrarily high accuracy, are different from the exact dispersion energies, whereas the CKS ones are potentially exact, i.e., would be exact to within numerical uncertainties if the exact DFT/TD-DFT descriptions of monomers were known ("exact" DFT calculations for small systems can be performed by utilizing an inversion of wave-function-based quantities and such an approach has been applied to interactions of small monomers[120,121]). Interestingly, the use of CKS versus UCKS response functions for the induction component makes relatively small difference in the results. Nevertheless, the former ones are used since they are potentially exact.

SAPT(DFT) can be implemented using density-fitting techniques[24,27,114,122]. The required computational effort scales then as $O(N^5)$, where N is a measure of system size. The density-fitted algorithms have recently been enhanced, allowing SAPT(DFT) calculations for dimers with 200 atoms in bases of polarized quadruple-zeta quality and 400 atoms in bases of partly augmented, polarized double-zeta quality[42].

In SAPT, the terms of the third- and higher-order in V are often approximated by the quantity

$$\delta E^{\mathrm{HF}}_{\mathrm{int,resp}} = E^{\mathrm{HF}}_{\mathrm{int}} - E^{(10)}_{\mathrm{elst}} - E^{(10)}_{\mathrm{exch}} - E^{(20)}_{\mathrm{ind,resp}} - E^{(20)}_{\mathrm{exch-ind,resp}}, \tag{7}$$

where $E^{\mathrm{HF}}_{\mathrm{int}}$ is the counterpoise-corrected supermolecular HF interaction energy. Since the supermolecular HF approach reproduces the first-order effects plus the induction and exchange-induction effects to all orders, $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ is an approximation for the two latter effects in the third and higher orders. The addition of $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ to the second-order SAPT interaction energies results in a hybrid perturbational plus supermolecular approach, but since $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ is reasonably small in most cases of practical interest and since it does have a well-defined physical interpretation, the use of $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ does not decrease the physical insights of SAPT. The addition of $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ is not fully rigorous, but it is recommended for polar monomers[107,108,123].

The second- and third-order SAPT exchange terms have initially been implemented using the so-called S^2 approximation[53], i.e., keeping in the antisymmetrizer only the permutations that exchange one electron from monomer A with one electron from monomer B (single-exchange approximation). This leads to expressions that include only terms proportional to the squares of overlap integrals between molecular orbitals of different monomers[53]. This approximation works well in the majority of cases, but at short intermonomer distances it may break down. Schäffer and Jansen derived and implemented expressions not involving this approximation for the second-order exchange-induction[124] and exchange-dispersion[125] corrections. Recently, Waldrop and Patkowski[126] presented an implementation of the third-order exchange-induction energy without the S^2 approximation.

III. PHYSICAL INTERPRETATION OF SAPT COMPONENTS

As mentioned in the Introduction, each SAPT component has a transparent and unique physical interpretation. Below, this is demonstrated term-by-term by analyzing SAPT formulas.

A. Electrostatic interaction

We start from the first-order energy, given by

$$E^{(1)} = \frac{\langle \Psi_0^A \Psi_0^B | V \mathcal{A} | \Psi_0^A \Psi_0^B \rangle}{\langle \Psi_0^A \Psi_0^B | \mathcal{A} | \Psi_0^A \Psi_0^B \rangle} = E^{(1)}_{\text{elst}} + E^{(1)}_{\text{exch}} \tag{8}$$

where $\mathcal{A}$ is the all-electron antisymmetrizer, Ψ_0^X is the ground-state wave function of monomer X, and

$$E^{(1)}_{\text{elst}} = \langle \Psi_0^A \Psi_0^B | V | \Psi_0^A \Psi_0^B \rangle \tag{9}$$

assuming that the wave functions are normalized [with the electrostatic energy given explicitly by Eq. (9), the first-order exchange energy, $E^{(1)}_{\text{exch}}$, is defined by $E^{(1)} - E^{(1)}_{\text{elst}}$]. The explicit form of the operator V is

$$\begin{aligned} V &= \sum_{i\in A}\sum_{j\in B} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_{i\in A} v^B(\boldsymbol{r}_i) + \sum_{j\in B} v^A(\boldsymbol{r}_j) + \sum_{\alpha\in A}\sum_{\beta\in B} \frac{Z_\alpha Z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|} \\ &= V_{\text{ee}} + V^B + V^A + V_0 \end{aligned} \tag{10}$$

where $\boldsymbol{r}_k$ and $\boldsymbol{R}_\gamma$ are positions of electrons and of nuclei, respectively, Z_γ are charges of nuclei, and

$$v^X(\boldsymbol{r}) = -\sum_{\gamma\in X} \frac{Z_\gamma}{|\boldsymbol{r} - \boldsymbol{R}_\gamma|} \tag{11}$$

is the electrostatic potential of the nuclei of monomer X times the electron charge. The operators listed in the last formula of Eq. (10) denote the consecutive terms in the preceding formula. Since the operator V depends at the most on the coordinates of one electron from monomer A and one electron from monomer B, one can perform integration over the coordinates of the remaining electrons in Eq. (9) and express the electrostatic energy in terms of electron densities ρ_X of monomers (normalized to the number of electrons, N_X)

$$E^{(1)}_{\rm elst} = \iint \frac{\rho_A(\boldsymbol{r}_1)\rho_B(\boldsymbol{r}_2)}{r_{12}}\, d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2 + \int v^B(\boldsymbol{r})\rho_A(\boldsymbol{r})\, d^3\boldsymbol{r} + \int v^A(\boldsymbol{r})\rho_B(\boldsymbol{r})\, d^3\boldsymbol{r} + V_0, \tag{12}$$

where $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$. This form of the electrostatic energy shows immediately that this quantity results from the Coulomb interactions between unperturbed monomers: between the electron densities, between the electron density of a monomer and the nuclear charges of the other monomer, and between the nuclear charges. Alternatively, one can express $E^{(1)}_{\rm elst}$ in the form

$$E^{(1)}_{\rm elst} = \iint \frac{\rho^{\rm tot}_A(\boldsymbol{r}_1)\rho^{\rm tot}_B(\boldsymbol{r}_2)}{r_{12}}\, d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2, \tag{13}$$

where

$$\rho^{\rm tot}_X(\boldsymbol{r}) = -\rho_X(\boldsymbol{r}) + \sum_{\gamma\in X} Z_\gamma \delta(\boldsymbol{r} - \boldsymbol{R}_\gamma), \tag{14}$$

showing that Eq. (9) indeed represents the electrostatic interaction energy between the total charge densities $\rho^{\rm tot}_X(\boldsymbol{r})$ of monomers. The large-R asymptotic expansion of $E^{(1)}_{\rm elst}$ is discussed in Sec. III E.

B. Induction interaction

The induction energy appears in the second order of RSPT

$$E^{(2)}_{\rm RS} = E^{(2)}_{\rm ind} + E^{(2)}_{\rm disp}.$$

It is separated from the dispersion energy as the contribution that includes excitations only on one of the monomers, i.e., the induction energy of system A perturbed by system B is given by

$$E^{(2)A\leftarrow B}_{\rm ind} = -\sum_{k\neq 0} \frac{|\langle \Psi^A_0 \Psi^B_0 | V | \Psi^A_k \Psi^B_0\rangle|^2}{E^A_k - E^A_0} = -\sum_{k\neq 0} \frac{|\langle \Psi^A_0 | \Omega_B | \Psi^A_k\rangle|^2}{E^A_k - E^A_0} = \langle \Psi^A_0 | \Omega_B | \Psi^{(1)A}_{\rm ind}\rangle \tag{15}$$

where Ψ_k^X (E_k^X) are the exact wave functions (energies) of monomers and the operator Ω_B can be expressed as

$$\Omega_B = \langle\Psi_0^B| \sum_{i\in A, j\in B} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} |\Psi_0^B\rangle + \sum_{i\in A} v^B(\boldsymbol{r}_i) = \sum_{i\in A} \omega^B(\boldsymbol{r}_i). \tag{16}$$

Note that ω^B is the electrostatic potential energy of unperturbed monomer B

$$\omega^B(\boldsymbol{r}) = -\int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\, \rho_B^{\text{tot}}(\boldsymbol{r}')\, d^3\boldsymbol{r}'. \tag{17}$$

The function $\Psi_{\text{ind}}^{(1)A}$ is the first-order induction wave function of monomer A, defined by the equation

$$(H_A - E_0^A)\Psi_{\text{ind}}^{(1)A} = \left(\langle\Psi_0^A|\Omega_B|\Psi_0^A\rangle - \Omega_B\right)\Psi_0^A \tag{18}$$

or by the equivalent spectral expansion

$$\Psi_{\text{ind}}^{(1)A} = -\sum_{k\neq 0} \frac{\langle\Psi_k^A|\Omega_B|\Psi_0^A\rangle}{E_k^A - E_0^A}\Psi_k^A. \tag{19}$$

[Our notation is consistent with that of Ref. 107, while there is sign mistake in Eq. (16) of Ref. 53]. The second formula in Eq. (15) results from the first one since due to the form of V and due to the fact that only the ground-state wave function of monomer B is involved, one can integrate over the coordinates of all electrons of monomer B. An analogous expression can be written for $E_{\text{ind}}^{(2)B\leftarrow A}$, so that $E_{\text{ind}}^{(2)} = E_{\text{ind}}^{(2)A\leftarrow B} + E_{\text{ind}}^{(2)B\leftarrow A}$.

While Eq. (15) shows already that the induction energy is due to the perturbation of monomer A by the electric field of unperturbed monomer B, a further insight can be achieved if this equation is expressed in terms of electron densities. To this end, consider the electron density of monomer A computed with the wave function

$$\Psi^A = \Psi_0^A + \Psi_{\text{ind}}^{(1)A}. \tag{20}$$

The induced electron density of the first-order, $\rho_{\text{ind}}^{(1)A}(\boldsymbol{r})$, is then given by

$$\rho_{\text{ind}}^{(1)A}(\boldsymbol{r}) = 2N_A \sum_{s,s_2,\ldots,s_N} \int \Psi_0^A(\boldsymbol{x},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_{N_A})\Psi_{\text{ind}}^{(1)A}(\boldsymbol{x},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_{N_A}) d^3\boldsymbol{r}_2\ldots d^3\boldsymbol{r}_{N_A}, \tag{21}$$

where $\boldsymbol{x}_i$ denotes space plus spin electron coordinates, the summation is over spins, and we assumed that the wave functions are real. Multiplying both sides of Eq. (21) by $\omega^B(\boldsymbol{r})$, integrating over $\boldsymbol{r}$, and comparing with the right-most side of Eq. (15), one can see that

$$E_{\text{ind}}^{(2)A\leftarrow B} = \frac{1}{2}\int \rho_{\text{ind}}^{(1)A}(\boldsymbol{r})\,\omega^B(\boldsymbol{r}) d^3\boldsymbol{r} = -\frac{1}{2}\iint \rho_{\text{ind}}^{(1)A}(\boldsymbol{r}_1)\frac{1}{r_{12}}\rho_B^{\text{tot}}(\boldsymbol{r}_2) d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2. \tag{22}$$

Equations (15) and (22) show that the response of monomer A to the perturbation by the potential Ω_B of the unperturbed monomer B results in the density deformation $\rho_{\rm ind}^{(1)A}(\boldsymbol{r})$. This deformation interacts with $\rho_B^{\rm tot}(\boldsymbol{r})$, but this is not just the standard Coulomb interaction since the latter would not have included the factor 1/2. An analogous term results from the interaction of $\rho_{\rm ind}^{(1)B}(\boldsymbol{r})$ with $\rho_A^{\rm tot}(\boldsymbol{r})$.

In the so-called polarization model of induction used in some force fields, the presence of the factor 1/2 in the expression for the polarization energy is explained as due to the energy needed for the creation of induced multipoles. This interpretation can be justified by the following quantum mechanical arguments (but such interpretation is not needed for the derivation presented above). Since Ψ^A of Eq. (20) is the wave function of molecule A in the electric field generated by the external potential Ω_B, the total energy of the perturbed system A is given through second order by the expectation value expression

$$E_{\rm tot}^A = \frac{\langle \Psi^A | H_0^A + \Omega_B | \Psi^A \rangle}{\langle \Psi^A | \Psi^A \rangle} = \frac{\langle \Psi^A | H_0^A \Psi^A \rangle}{\langle \Psi^A | \Psi^A \rangle} + \langle\, \Psi_0^A | \Omega_B | \Psi_0^A \,\rangle + 2\langle \Psi_0^A | \Omega_B \Psi_{\rm ind}^{(1)A} \rangle + \mathcal{O}(V^3). \tag{23}$$

The first term on the right-hand-side is the total energy of molecule A (using the Hamiltonian of an *isolated* molecule A) described by the wave function Ψ^A. By virtue of the variation principle, this energy is higher than $E_0^A = \langle\, \Psi_0^A | H_0^A \Psi_0^A \,\rangle$. The difference $\langle \Psi^A | H_0^A \Psi^A \rangle \langle \Psi^A | \Psi^A \rangle^{-1} - E_0^A$ can be interpreted as the energy needed to polarize the molecule. In view of Eq. (15) [or Eq. (22)], the last term in Eq. (23) is equal to the Coulomb interaction of the electron density induced on A by the unperturbed charge density of monomer B with the total unperturbed density of monomer B, i.e., to $2E_{\rm ind}^{(2)A\leftarrow B}$. One can now write (still through second order)

$$\frac{\langle \Psi^A | H_0^A \Psi^A \rangle}{\langle \Psi^A | \Psi^A \rangle} - E_0^A = \langle \Psi_{\rm ind}^{(1)A} | (H_0^A - E_0^A) \Psi_{\rm ind}^{(1)A} \rangle = -\langle \Psi_{\rm ind}^{(1)A} | \Omega_B \Psi_0^A \rangle, \tag{24}$$

where we used the first-order perturbation equation (18). Thus, the energy needed to polarize a molecule is equal to exactly half of the negative of Coulomb's interaction of the induced electron density with the unperturbed total charge distribution of the interacting partner.

One may add here that the third-order induction energy of SAPT, $E_{\rm ind}^{(3)}$, has also been considered in the literature, see Sec. II.B.2 in Ref. 53 and a more extensive discussion of this subject in Ref. 107. This formula for $E_{\rm ind}^{(3)}$ (see Eq. (A.22) in the Appendix) was implemented with neglect of intramonomer correlation in the nonresponse[107] and the response formulation[108]. The published formula for $E_{\rm ind}^{(3)}$ is expressed in terms of only the zerothand first-order wave functions using the $2n+1$ rule. To provide an alternative physical interpretation of $E^{(3)}_{\rm ind}$, we have derived two new formulas for this quantity, expressing it in terms of the second-order wave functions, see Appendix. In particular, formula (A.27) can be written in terms of densities as

$$E^{(3)}_{\rm ind} = \frac{1}{2}\int \bar{\rho}^{(02)A}_{\rm ind}(\boldsymbol{r})\omega^B(\boldsymbol{r})d^3\boldsymbol{r} + \frac{1}{2}\int \bar{\rho}^{(02)B}_{\rm ind}(\boldsymbol{r})\omega^A(\boldsymbol{r})d^3\boldsymbol{r} + \iint \rho^{(1)A}_{\rm ind}(\boldsymbol{r}_1)\frac{1}{r_{12}}\rho^{(1)B}_{\rm ind}(\boldsymbol{r}_2)d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2, \tag{25}$$

where $\bar{\rho}^{(02)A}_{\rm ind}(\boldsymbol{r})$ is defined by Eq. (21) with $\Psi^{(1)A}_{\rm ind}$ replaced by the second-order induction function given by Eq. (A.24) in the Appendix. The superscript "02" indicates that this is the component of the second-order density that originates from the product of the zeroth- and second-order induction functions, cf. Eq. (A.21). Note again the factor 1/2 multiplying the Coulomb interaction of the second-order charge density $\bar{\rho}^{(02)A}_{\rm ind}(\boldsymbol{r})$ with the electrostatic potential $\omega^B(\boldsymbol{r})$ in the first term, and analogously in the second term. There is no such factor in the third term that describes the interaction of the first-order density on A with its analogue on B.

In contrast to the dispersion interaction that will be discussed in the next subsection, the induction interaction does not involve any intermonomer electron correlation. To see this, let us consider, as the simplest possible example, the interaction involving the hydrogen atom and a hydrogenlike ion or a one-electron molecular ion. The lowest-order dimer's wave function describing the induction interaction is the product of function (20) and of an analogous function for monomer B

$$\begin{aligned}\Psi_{\rm ind}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= \Psi^A(\boldsymbol{r}_1)\Psi^B(\boldsymbol{r}_2)\\ &= \Psi^A_0(\boldsymbol{r}_1)\Psi^B_0(\boldsymbol{r}_2) + \Psi^{(1)A}_{\rm ind}(\boldsymbol{r}_1)\Psi^B_0(\boldsymbol{r}_2) + \Psi^A_0(\boldsymbol{r}_1)\Psi^{(1)B}_{\rm ind}(\boldsymbol{r}_2)\\ &+ \Psi^{(1)A}_{\rm ind}(\boldsymbol{r}_1)\Psi^{(1)B}_{\rm ind}(\boldsymbol{r}_2).\end{aligned} \tag{26}$$

Since we consider one-electron monomers and since RSPT does not impose permutational symmetry, we could trivially sum out the spin variable. Since the induction wave function is in a product form, it is immediately clear that there is no intermonomer electron correlation. Nevertheless, to prepare for the discussion of dispersion interactions, let us show this fact explicitly. The probability density of finding electron 1 at $\boldsymbol{r}_1$ and electron 2 at $\boldsymbol{r}_2$ equals $\Psi^A(\boldsymbol{r}_1)^2\Psi^B(\boldsymbol{r}_2)^2$, while the conditional probability density $P_{\rm ind}(\boldsymbol{r}_1|\boldsymbol{r}_2)$ of finding electron 1 at $\boldsymbol{r}_1$ knowing that electron 2 was found at $\boldsymbol{r}_2$ is given by

$$P_{\rm ind}(\boldsymbol{r}_1|\boldsymbol{r}_2) = \frac{\big[\Psi_{\rm ind}(\boldsymbol{r}_1,\boldsymbol{r}_2)\big]^2}{\int\big[\Psi_{\rm ind}(\boldsymbol{r}_1,\boldsymbol{r}_2)\big]^2 d^3\boldsymbol{r}_1} = \frac{\big[\Psi_0^A(\boldsymbol{r}_1)+\Psi_{\rm ind}^{(1)A}(\boldsymbol{r}_1)\big]^2}{1+\int\big[\Psi_{\rm ind}^{(1)A}\big]^2(\boldsymbol{r}_1)d^3\boldsymbol{r}_1}. \tag{27}$$

Clearly, this conditional probability is independent of $\boldsymbol{r}_2$, hence $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are independent random variables. In fact, the wave function corresponding to the infinite-order induction interaction is the product of functions $\Psi_{\rm ind}^A\,\Psi_{\rm ind}^B$ depending on electronic coordinates of A and B, respectively, see the Appendix, so these coordinates are uncorrelated, independent random variables. Of course, in the case of the induction interaction of many-electron systems, the correlation of electronic motion within A (or within B), i.e., the *intramonomer* correlation, is always present and cannot be neglected, see Sec. VI.B.3 in Ref. 53.

C. Dispersion interaction

The remaining part of the second-order RSPT interaction energy is the dispersion energy involving excitations on both monomers:

$$E_{\rm disp}^{(2)} = -\sum_{m\neq 0}\sum_{n\neq 0}\frac{|\langle\Psi_0^A\Psi_0^B|V|\Psi_m^A\Psi_n^B\rangle|^2}{E_m^A+E_n^B-E_0^A-E_0^B} = \langle\Psi_0^A\Psi_0^B|V|\Psi_{\rm disp}^{(1)}\rangle = \langle\Psi_0^A\Psi_0^B|V_{\rm ee}|\Psi_{\rm disp}^{(1)}\rangle, \tag{28}$$

where the first-order dispersion function $\Psi_{\rm disp}^{(1)}$ is defined as

$$\Psi_{\rm disp}^{(1)} = -\sum_{m\neq 0}\sum_{n\neq 0}\frac{\langle\Psi_m^A\Psi_n^B|V|\Psi_0^A\Psi_0^B\rangle}{E_m^A+E_n^B-E_0^A-E_0^B}\Psi_m^A\Psi_n^B. \tag{29}$$

Note that due to the orthogonality of wave functions, only the electron-electron repulsion part of V makes a contribution to $E_{\rm disp}^{(2)}$.

The dispersion interaction is more difficult to interpret than the electrostatic and induction interactions since it is a purely quantum phenomenon that does not have a classical equivalent. Moreover, the mechanism of this interaction is different at the long range and at intermediate intermolecular distances, where the electron densities of monomers begin to overlap. The basic new physics that lies at the origin of the dispersion interaction is the *intermonomer* electron correlation, i.e., the correlation of electronic positions in one monomer with those in the interacting partner. As discussed in the previous subsection, this correlation is absent in the wave function used to describe the induction interaction.

To show the connection of the intermonomer electron correlation with the dispersion interaction, we consider a system of two hydrogen atoms. At large interatomic distances R, the interaction operator V can then be represented by[62]

$$V = -(2z_1z_2 - x_1x_2 - y_1y_2)\,R^{-3} + \mathcal{O}(R^{-4}), \tag{30}$$

where atom A is at the center of coordinate system, atom B is at R on the z axis, x_i, y_i, z_i, $i = 1, 2$, are the coordinates of electrons measured in Cartesian systems located on atoms (electron 1 on A and 2 on B). If the operator V is restricted to the first term, $\sim 1/R^3$, the sum in Eq. (29) reduces (due to symmetry of the system) to orbitals with the angular momentum quantum number $l = 1$ (and an arbitrary principal quantum number) only, i.e., the excited wave function products $\Psi_k^A\,\Psi_l^B$ can be only of the p_zp_z, p_xp_x, and p_yp_y type. It will be convenient to write each such function as including Ψ_0^X, i.e., the $1s$ orbital, as a factor, for example,

$$\psi_{n10}(\boldsymbol{r}_1) = z_1 f_n(r_1)\Psi_0^A(r_1)$$

where $r_i = |\boldsymbol{r}_i|$, $i = 1, 2$. Redefining the summation indices, Eq. (29) can be written as

$$\begin{aligned}\Psi^{(1)}_{\text{disp}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = -\sum_{m\neq 0}\sum_{n\neq 0} \big[&c^{xx}_{mn}x_1f_m(r_1)x_2f_n(r_2) + c^{yy}_{mn}y_1f_m(r_1)y_2f_n(r_2) \\ &+ c^{zz}_{mn}z_1f_m(r_1)z_2f_n(r_2)\big]\Psi_0^A(r_1)\Psi_0^B(r_2) + \mathcal{O}(R^{-4}).\end{aligned} \tag{31}$$

For the z_1z_2 term, the linear coefficient can be written in the form

$$c^{zz}_{mn} = -\frac{2}{R^3}\frac{\langle\,\Psi_0^A|z_1^2f_m\Psi_0^A\,\rangle\langle\,\Psi_0^B|z_2^2f_n\Psi_0^B\,\rangle}{E_m^A + E_n^B - E_0^A - E_0^B} = -\frac{2}{R^3}d^{zz}_{mn}$$

while $c^{xx}_{mn} = c^{yy}_{mn} = -c^{zz}_{mn}/2$. This allows one to pull the x, y, and z coordinates out of the sum

$$\begin{aligned}\Psi^{(1)}_{\text{disp}}(\boldsymbol{r}_1, \boldsymbol{r}_2) &= (2z_1z_2 - x_1x_2 - y_1y_2)\Psi_0^A(r_1)\Psi_0^B(r_2)\frac{1}{R^3}\sum_{m\neq 0}\sum_{n\neq 0} d^{zz}_{mn}f_m(r_1)f_n(r_2) + \mathcal{O}(R^{-4}) \\ &= (2z_1z_2 - x_1x_2 - y_1y_2)\Psi_0^A(r_1)\Psi_0^B(r_2)\frac{1}{R^3}F(r_1, r_2) + \mathcal{O}(R^{-4}).\end{aligned} \tag{32}$$

The function $F(r_1, r_2)$ is positive at least for small r_1 and r_2. This follows from Eq. (28) since the dispersion energy is always negative:

$$\begin{aligned}E^{(2)}_{\text{disp}} = \big\langle\Psi_0^A\Psi_0^B|V|\Psi^{(1)}_{\text{disp}}\big\rangle = -\langle\Psi_0^A(r_1)\Psi_0^B(r_2)|&\frac{(2z_1z_2 - x_1x_2 - y_1y_2)^2}{R^6}F(r_1, r_2)\Psi_0^A(r_1)\Psi_0^B(r_2)\big\rangle \\ &+ \mathcal{O}(R^{-8}).\end{aligned} \tag{33}$$

It is now clear that the total function accounting for the dispersion interaction

$$\Psi_{\rm disp}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \Psi_0^A(r_1)\, \Psi_0^B(r_2) + \Psi_{\rm disp}^{(1)}(\boldsymbol{r}_1, \boldsymbol{r}_2), \tag{34}$$

cannot be represented as a product of functions depending on $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The conditional probability density $P_{\rm disp}(\boldsymbol{r}_1|\boldsymbol{r}_2)$ of finding electron 1 at $\boldsymbol{r}_1$ while electron 2 is fixed at $\boldsymbol{r}_2$ is now given by

$$P_{\rm disp}(\boldsymbol{r}_1|\boldsymbol{r}_2) = \left[\Psi_0^A(r_1)\right]^2 \left[1 + 2\,(2z_1z_2 - x_1x_2 - y_1y_2)\, F(r_1, r_2) R^{-3}\right] + \mathcal{O}(R^{-4}), \tag{35}$$

where we used the fact that $\int \Psi_0^A \Psi_{\rm disp}^{(1)}(\boldsymbol{r}_1, \boldsymbol{r}_2) d^3\boldsymbol{r}_1 = 0$. We see that for a system described by the function $\Psi_{\rm disp}(\boldsymbol{r}_1, \boldsymbol{r}_2)$, the positions of electrons are correlated. The probability of finding electron 1 at $\boldsymbol{r}_1$ does depend on the position of electron 2. There is an increased probability if the electrons are on the opposite sides of the internuclear axis (when the products x_1x_2 and y_1y_2 are negative) and if both z_i are positive, i.e., one electron is between the nuclei and another is outside (in-out configuration).

A quantitative measure of correlation of random variables X and Y is their covariance $\langle X, Y\rangle_{\rm c} = \langle (X - \langle X\rangle)(Y - \langle Y\rangle)\rangle$, where $\langle \cdots \rangle$ denotes the expectation value computed with an appropriate probability density. Using $\left[\Psi_{\rm disp}(\boldsymbol{r}_1, \boldsymbol{r}_2)\right]^2$ as this probability density, we find that the covariance of the random variables z_1 and z_2 in the considered system is

$$\langle z_1, z_2\rangle_{\rm c} = 2 \iint \Psi_0^A(\boldsymbol{r}_1)\Psi_0^B(\boldsymbol{r}_2)\, z_1\, z_2\, \Psi_{\rm disp}^{(1)}(\boldsymbol{r}_1, \boldsymbol{r}_2)\, {\rm d}^3\boldsymbol{r}_1 {\rm d}^3\boldsymbol{r}_2 + \mathcal{O}(R^{-9}), \tag{36}$$

where the strong orthogonality property was used again. An analogous result holds for $\langle x_1, x_2\rangle_{\rm c}$ and for $\langle y_1, y_2\rangle_{\rm c}$. Applying these relations in Eq. (33), the dispersion energy can be directly expressed through covariances

$$E_{\rm disp}^{(2)} = -\frac{1}{2}\left[\, 2\,\langle z_1, z_2\rangle_{\rm c} - \langle x_1, x_2\rangle_{\rm c} - \langle y_1, y_2\rangle_{\rm c}\,\right] R^{-3} + \mathcal{O}(R^{-8}). \tag{37}$$

Due to spherical symmetry of monomers, $\langle x_1, x_2\rangle_{\rm c} = \langle y_1, y_2\rangle = -\langle z_1, z_2\rangle_{\rm c}/2$, the dispersion energy can be expressed in an even simpler form

$$E_{\rm disp}^{(2)} = -\frac{3}{2}\,\langle z_1, z_2\rangle_{\rm c}\, R^{-3} + \mathcal{O}(R^{-8}). \tag{38}$$

One can further express $E_{\rm disp}^{(2)}$ through the dimensionless correlation coefficient C_{XY} defined as $\langle X, Y\rangle_c/(\sigma_X\sigma_Y)$, where $\sigma_X = \sqrt{\langle\, X^2 - \langle\, X\,\rangle^2\,\rangle}$ is the standard deviation of variable X. In our case, $\sigma_{z_1} = \sqrt{\langle\, z_1^2\,\rangle}$. C_{XY} equals 1 for perfectly correlated, -1 for perfectly anticorrelated, and vanishes for independent random variables (the opposite is not true). Using these relations, we can write

$$E^{(2)}_{\rm disp} = -\frac{3}{2}\, C_{z_1 z_2}\, \sqrt{\langle z_1^2\rangle}\sqrt{\langle z_2^2\rangle}\, R^{-3} + \mathcal{O}(R^{-8}). \tag{39}$$

This equation shows that at long range the magnitude of the dispersion energy is proportional to the correlation coefficient for the projections of the vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ on the interaatomic axis and to the standard deviations $\langle z_i^2\rangle^{1/2}$ measuring the spread of these variables around zero.

We have shown that at large R the electrons are more likely to be both on the right or both on the left of their nuclei when looking perpendicularly to the interatomic axis. However, this interpretation changes at distances of van der Waals minima and in the repulsive region where there is a significant overlap of monomer wave functions. To see this, we consider again the interaction of two hydrogen atoms. The first-order dispersion function can then be obtained by minimizing the following Hylleraas functional[21,127]

$$E^{(20)}_{\rm disp} \le J[\tilde{\Psi}^{(1)}_{\rm disp}] = \langle \tilde{\Psi}^{(1)}_{\rm disp} | H_A(\boldsymbol{r}_1) + H_B(\boldsymbol{r}_2) - E_0^A - E_0^B | \tilde{\Psi}^{(1)}_{\rm disp}\rangle + 2\langle \tilde{\Psi}^{(1)}_{\rm disp} | r_{12}^{-1} \Psi_0^A \Psi_0^B\rangle, \tag{40}$$

under the condition that the trial function $\tilde{\Psi}^{(1)}_{\rm disp}$ is orthogonal to $\Psi_k^A \Psi_0^B$ and to $\Psi_0^A \Psi_l^B$ for any k and l (i.e., that $\tilde{\Psi}^{(1)}_{\rm disp}$ is strongly orthogonal to $\Psi_0^A \Psi_0^B$). Since the quadratic term is always positive, minimization tends to keep $\tilde{\Psi}^{(1)}_{\rm disp}$ small in magnitude, at the same time making the linear term as large in magnitude a possible. Consider then two positions of electrons 1 and 2 — both positions on the axis connecting the nuclei and the same distance from the closest nuclei, but in one case both electrons are inside while in the other case both are outside of the dimer. Since the product of orbitals has the same value in both cases, the value of the function in the ket of the linear term is larger for the inside configuration. Consequently, the dispersion function will also be larger in this case than for the outside case. This picture is in disagreement with the one valid at large distances, but agrees with the numerical results obtained for intermolecular separations corresponding to van der Waals minima: the magnitude of the dispersion amplitude was found to be the largest in the region between atoms[128,129]. In fact, adequate representation of the dispersion functions in this region requires the use of dimer-centered basis sets[129], bond functions[129,130], or explicitly correlated bases[67,131–133].

An often used interpretation of the dispersion energy states that this energy is due to Coulomb interactions of instantaneous or fluctuating dipole moments on each monomer.

There are problems with this interpretation. First, a minor one, is that the words "instantaneous" and "fluctuating" imply a time dependence, whereas there is no time dependence in Eq. (28): the dispersion energy appears in time-independent quantum mechanics. A reason for introducing time dependence in this interpretation could be that although the dimer is in a stationary state, each electron is assumed to have a definitive position at each instant of time. However, the physical origins of dispersion energy can be discussed according to the generally-accepted Copenhagen interpretation of quantum mechanics which says that the only knowledge about an electron is the probability density of finding it at a point in space, given by the square of the magnitude of wave function (for stationary states, this probability density is independent of time). Accordingly, one can disregard the time connotations and view the dipole moments considered in the discussed interpretation of dispersion interaction as formed by an electron and the nucleus, where the position of the electron is just a set of fixed values of coordinates in a time-independent wave function. Then, in the case of two interacting hydrogen atoms, if one electron is at $\boldsymbol{r}_1$ measured from nucleus A, it forms a dipole moment $\boldsymbol{\mu}_1 = q\boldsymbol{r}_1$, where q is the electron charge. Similarly, if the other electron is at $\boldsymbol{r}_2$ relative to nucleus B, it forms a dipole moment $\boldsymbol{\mu}_2$. These dipole moments interact as $\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2/R^3 - 3(\boldsymbol{\mu}_1 \cdot \boldsymbol{R})\,(\boldsymbol{\mu}_2 \cdot \boldsymbol{R})/R^5$. This R-dependence is, however, different than that of the dispersion interaction, which decays as $1/R^6$, and moreover the interaction of the dipole moments defined in this way would average to zero for two hydrogen atoms. Thus, the interpretation discussed here does not uncover the essential mechanism of the dispersion interactions which results from correlations between these positions. Another version of this interpretation states that the dispersion energy is due to the interaction of a fluctuating dipole moment on one monomer with the dipole moment induced by this fluctuating dipole on the other monomer, leading to the interaction energy decaying as $1/R^6$. However, this model does not predict the correct value of the dispersion coefficient C_6, as it implies a linear dependence on the monomer polarizability.

D. Exchange interactions

The first-order exchange energy $E^{(1)}_{\text{exch}}$ is defined via Eqs. (8) and (9). Neglecting the double and higher multiple electron exchanges between monomers, the antisymmetrizer can be written as

$$\mathcal{A} \approx (1+\mathcal{P}_1)\mathcal{A}_A\mathcal{A}_B \tag{41}$$

where $\mathcal{A}_X$ is the antisymmetrizer for monomer X and $\mathcal{P}_1$ is the single-exchange operator. i.e., the sum of the operators P_{ij} that exchange the coordinates of the ith and jth electron in the wave function

$$\mathcal{P}_1 = -\sum_{i\in A}\sum_{j\in B} P_{ij}. \tag{42}$$

Using the approximate form of $\mathcal{A}$, one obtains the first-order exchange energy in the so-called S^2 approximation

$$E^{(1)}_{\mathrm{exch}}(S^2) = \langle V\mathcal{P}_1\rangle - \langle V\rangle\langle\mathcal{P}_1\rangle, \tag{43}$$

where $\langle\cdots\rangle$ denotes the expectation value computed with the wave function $\Psi_0^A\Psi_0^B$, Note that we assume that the monomers' wave functions are antisymmetric, so that $\mathcal{A}_X\Psi_0^X = \Psi_0^X$. The name "$S^2$ approximation" results from the fact that each term in Eq. (43) is proportional to the second power of intermonomer orbital overlap integrals. To see this, represent the wave functions Ψ_0^X by their FCI expansions. The $\langle\mathcal{P}_1\rangle$ factor in Eq. (43) will contain contributions of the type

$$\begin{aligned}
&\langle \ldots \phi_k^A(\boldsymbol{x}_i)\ldots\phi_l^B(\boldsymbol{x}_j)\ldots|P_{ij}\ldots\phi_{k'}^A(\boldsymbol{x}_i)\ldots\phi_{l'}^B(\boldsymbol{x}_j)\ldots\rangle\\
&=\langle \ldots \phi_k^A(\boldsymbol{x}_i)\ldots\phi_l^B(\boldsymbol{x}_j)\ldots|\ldots\phi_{k'}^A(\boldsymbol{x}_j)\ldots\phi_{l'}^B(\boldsymbol{x}_i)\ldots\rangle\\
&=\langle \phi_k^A(\boldsymbol{x}_i)|\phi_{l'}^B(\boldsymbol{x}_i)\rangle\langle \phi_{k'}^A(\boldsymbol{x}_j)|\phi_l^B(\boldsymbol{x}_j)\rangle\ldots,
\end{aligned} \tag{44}$$

where ϕ_k^X are occupied or virtual spinorbitals of monomer X. While $\langle\mathcal{P}_1\rangle$ produces explicit S^2 terms, the term $\langle V\mathcal{P}_1\rangle$ produces electron repulsion and nuclear attraction integrals which are proportional to these overlap integrals. Since such integrals decay exponentially with R, $E^{(1)}_{\mathrm{exch}}(S^2)$ becomes negligible at R a few times larger than the van der Waals minimum distance.

The second-order energy formula in the SRS method[2] is

$$E^{(2)} = \left[\langle \Psi_0^A\Psi_0^B|V\mathcal{A}\Psi^{(1)}_{\mathrm{RS}}\rangle - E^{(1)}\langle \Psi_0^A\Psi_0^B|\mathcal{A}\Psi^{(1)}_{\mathrm{RS}}\rangle\right] / \langle \Psi_0^A\Psi_0^B|\mathcal{A}\Psi_0^A\Psi_0^B\rangle. \tag{45}$$

After replacing $\mathcal{A}$ by its single-exchange approximation and keeping only terms proportional to $\mathcal{P}_1$, one gets the following formulas for the exchange-induction and exchange-dispersion energies[53]

$$E^{(2)A\leftarrow B}_{\rm exch-ind}(S^2) = \langle \Psi_0^A \Psi_0^B |\, (V - \langle V \rangle)\, (\mathcal{P}_1 - \langle \mathcal{P}_1 \rangle)\, \Psi^{(1)A}_{\rm ind} \Psi_0^B \rangle. \tag{46}$$

and

$$E^{(2)}_{\rm exch-disp}(S^2) = \langle \Psi_0^A \Psi_0^B |\, (V - \langle V \rangle)\, (\mathcal{P}_1 - \langle \mathcal{P}_1 \rangle)\, \Psi^{(1)}_{\rm disp} \rangle. \tag{47}$$

Since the electrons in the induction and dispersion wave functions are localized in the same way as in $\Psi_0^A \Psi_0^B$, both second-order exchange corrections are proportional to squares of overlap integrals, similarly as in the first order. Consequently, these corrections decay exponentially with R.

For the interaction of closed-shell monomers, the first- and second-order corrections are positive and provide the short-range repulsive effect needed for correct physical behavior of potential energy surfaces. If these corrections were not included, the RSPT method through second order would give surfaces much too negative and not exhibiting repulsive walls. Similarly as the dispersion energies, the exchange energies do not have a classical analogue. They can be physically interpreted as a result of quantum tunneling of electrons through the potential barrier between monomers.

To see the relation between exchange interactions and quantum electron tunneling, we again consider two hydrogen atoms. At infinite separations R, electron 1 (electron 2) is residing in a potential well created by the nucleus of atom A (atom B). At any finite but large R, the potential due to nuclei acting on an electron is close to zero except near nuclei. Thus, there is broad potential barrier between the nuclear wells. If one of the electrons tunnels through the barrier, the other one has to tunnel in the opposite direction, exchanging places at the potential energy wells (both electrons cannot stay at the same nucleus because of the interelectronic repulsion). Thus, tunneling leads to electron exchange.

One might think that at very large R the electron 1 will mainly stay near nucleus A since the probability of tunneling is negligibly small for such a broad barrier, but this picture is not right since the electrons are indistinguishable in the SRS method and the SRS wave function is fully antisymmetric, as required by laws of quantum mechanics. Thus, for *any* R, the probability of finding electron 1 at nucleus B is the same as at nucleus A [since the potential energy of the electron in the field of nuclei is symmetric with respect of the interchange of nuclear positions, cf. Eq. (10)]. In fact, Ahlrichs[78] has rigorously proved that the spin-free parts of the exact wave functions behave asymptotically (at large R) as

$$\Psi_{\pm}(\boldsymbol{r}_1,\boldsymbol{r}_2)=\frac{1}{\sqrt{2}}\big[\Psi_0^A(\boldsymbol{r}_1)\,\Psi_0^B(\boldsymbol{r}_2)\pm\Psi_0^B(\boldsymbol{r}_1)\,\Psi_0^A(\boldsymbol{r}_2)\big]+\mathcal{O}(R^{-3}),\tag{48}$$

where the plus sign applies to the ground state singlet wave function (since it must be nodeless) and the minus sign to the lowest excited state triplet wave function. Through the first-order in V, the interaction energies obtained with these wave functions are equal to

$$E^{(1)}_{\mp}=E^{(1)}_{\text{elst}}\pm E^{(1)}_{\text{exch}},\tag{49}$$

where $E^{(1)}_{\text{elst}}$ is given by Eq. (9) and $E^{(1)}_{\text{exch}}$ by Eq. (43). The plus sign on the right-hand side is for the triplet state and the minus sign for the singlet state (since $E^{(1)}_{\text{exch}}$ is positive). Note that since Eq. (49) is of first order, it does not determine the correct large-R asymptotics of the exchange energy[134,135].

At large intermolecular distances, the energetic effect of electron tunneling, given by the exchange energy, vanishes exponentially and the knowledge of the RSPT wave function is sufficient to compute very accurate values of the interaction energy despite the exact wave function of the dimer differing dramatically from the RSPT one.

Another way to look at the exchange interactions is to calculate the conditional probability density of finding electron 1 at $\boldsymbol{r}_1$ when the position of electron 2 is fixed at $\boldsymbol{r}_2$. With the wave functions of Eq. (48), this probability density is given (at large R) by

$$P(\boldsymbol{r}_1\,|\,\boldsymbol{r}_2)=\frac{\big[\Psi_0^A(\boldsymbol{r}_1)\,\Psi_0^B(\boldsymbol{r}_2)\big]^2+\big[\Psi_0^B(\boldsymbol{r}_1)\,\Psi_0^A(\boldsymbol{r}_2)\big]^2}{\big[\Psi_0^A(\boldsymbol{r}_2)\big]^2+\big[\Psi_0^B(\boldsymbol{r}_2)\big]^2}+\mathcal{O}(R^{-3}),\tag{50}$$

where terms containing $\Psi_0^A(\boldsymbol{r}_i)\,\Psi_0^B(\boldsymbol{r}_i)$ are omitted since such product is everywhere close to zero. This expression shows that the positions of electrons are strongly correlated at large R. When electron 2 is in the vicinity of nucleus B, the second term in the numerator and the first term in the denominator are negligible so the probability density of finding electron 1 is localized at nucleus A, whereas when electron 2 is at nucleus A then electron 1 can be found most likely at nucleus B. This is the so-called "left-right" correlation. In contrast, with the RSPT zeroth-order function, $P(\boldsymbol{r}_1\,|\,\boldsymbol{r}_2)=[\Psi_0^A(\boldsymbol{r}_1)]^2$, i.e., the position of electron 1 is independent of the position of electron 2, the probability density of electron 1 is localized at nucleus A, and the probability of finding electron 1 at B is negligible.

We have seen that the correlation coefficient $C_{z_1z_2}$ calculated with the wave function of Eq. (32) decays as $1/R^3$ at infinity, as implied by Eq. (39). Since $C_{z_1z_2}=$

$\langle z_1, z_2\rangle_{\rm c}/\left(\sqrt{\langle z_1^2\rangle}\sqrt{\langle z_2^2\rangle}\right)$, its essential part is given by Eq. (36). If the integral in Eq. (36) is calculated with the exact wave function accounting for the tunneling, the additional terms all decay exponentially, therefore $C_{z_1z_2}$ calculated with the antisymmetrized wave function also decays as $1/R^3$. One can easily show that the covariance $\langle z_1, z_2\rangle$ computed with the wave function of Eq. (48) vanishes exponentially. This fact may be viewed as a paradox since, as shown by Eq. (50), the variables z_1 and z_2 remain strongly correlated at large R. If $\langle z_1, z_2\rangle$ is calculated with the exact wave function accounting for both the tunneling and dispersion, it also vanishes at large R, but in this case as $1/R^3$. This apparently paradoxical behavior is possible since vanishing of the covariance does not guarantee independence of random variables.

Another way of looking at the exchange interactions is to use time-dependent quantum mechanics. Since $\Psi_\pm$ are eigenfunctions of the dimer Hamiltonian H, their time evolution gives only a phase factor. However, if we prepare the system in a state $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t=0) = (\Psi_+ + \Psi_-)/\sqrt{2} = \Psi_0^A(\boldsymbol{r}_1)\,\Psi_0^B(\boldsymbol{r}_2) + \mathcal{O}(R^{-3})$, the time evolution will generate the exchange component. This is seen applying the identity $e^{-iHt}\Psi_\pm = e^{-iE_\pm t}\Psi_\pm + \mathcal{O}(R^{-3})$, which allows us to write the time evolution in the following form (except for an overall phase factor)

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \cos(E_{\rm exch}\, t)\,\Psi_0^A(\boldsymbol{r}_1)\,\Psi_0^B(\boldsymbol{r}_2) + i\,\sin(E_{\rm exch}\, t)\,\Psi_0^B(\boldsymbol{r}_1)\,\Psi_0^A(\boldsymbol{r}_2) + \mathcal{O}(R^{-3}), \quad (51)$$

where $E_{\rm exch} = (E_- - E_+)/2$ is the exact exchange energy. Equation (51) shows that after the time $\pi/(2E_{\rm exch})$ electrons exchange their places. After the time $\pi/E_{\rm exch}$, the probability distribution is again the same as at $t = 0$. One can say that electrons tunnel back and fourth [with frequency $\nu_{\rm exch} = E_{\rm exch}/(2\pi)$] between two resonance structures $\Psi_0^A(\boldsymbol{r}_1)\,\Psi_0^B(\boldsymbol{r}_2)$ and $\Psi_0^B(\boldsymbol{r}_1)\,\Psi_0^A(\boldsymbol{r}_2)$.

As stated earlier, the first- and second-order exchange contributions to interaction energies of closed-shell multielectron monomers are positive. Therefore, one often uses the term “exchange-repulsion energies” for these contributions. Another term used is “Pauli’s repulsion” since Pauli’s principle follows from the antisymmetrization postulate. A question to ask is why the exchange contributions are positive. In some publications, the following explanation resulting from Pauli’s principle is proposed: the electrons of atom A cannot penetrate the space of atom B and therefore are constrained spatially in their motion, which increases their (positive) kinetic energy. This explanation is not correct since, as it is clear from Eq. (48), all electrons have access to the same space. Furthermore, for the singlet state of H–H, the exchange contribution is actually negative.

For H–H, the explanation for the signs of the exchange contributions is simple: in the triplet state, spatial (spin-free) wave function has one more node than in the singlet state and in quantum mechanics the energy of a series of states generated by the same potential increases with the number of nodes. For multielectron monomers, the reasons are more subtle. Briefly, when one monomer has three or more electrons, the energy of the lowest physical, i.e., antisymmetric state lies well above the energy of the unphysical, Pauli-forbidden ground state[18]. Since RSPT semiconverges to the latter state and SRS semiconverges to the former state, the exchange contributions have to be positive for such systems. In fact, the physical ground state of the dimer lies in a Pauli-forbidden continuum of states[53,89,136], see Fig. 1 in Ref. 18. The reason that the physical state has a higher energy than unphysical ones is that it is the spin-free solution of Schrödinger's equation with the largest number of nodes among the states considered. For interactions of open-shell atoms, the exchange contribution to the interaction energy can be negative (attractive), leading to formation of a covalent bond[18].

For some purposes, it is convenient to group togther the second-order RSPT and exchange contributions, although, as discussed above, the induction and dispersion interactions have different physical origins from their exchange counterparts, so from the point of view of physical interpretation the two types of terms should be considered separately. However, when developing potential energy surfaces, it is often convenient to clamp them together and fit analytically the composite contributions

$$E^{(2)}_{\mathrm{indx}} = E^{(2)}_{\mathrm{ind}} + E^{(2)}_{\mathrm{exch-ind}} \qquad E^{(2)}_{\mathrm{dispx}} = E^{(2)}_{\mathrm{disp}} + E^{(2)}_{\mathrm{exch-disp}}. \tag{52}$$

Adding exponentially decaying exchange terms to the RSPT terms decaying at the long range as inverse powers of R does not lead to conceptual problems since the RSPT components in fact also have purely exponential contributions, due to charge overlaps[53,79–82] at small R. Such addition is particularly convenient for the induction terms since the induction energy becomes very different from its asymptotic expansion in the region of the van der Waals minimum[84] and the addition of the exchange-induction terms improves the agreement between the two quantities. Some authors[137], argued that such addition should also be performed in the first order for the purpose of physical interpretation. One more advantage of such additions is that since essentially all electronic structure methods used in the supermolecular approach apply globally antisymmetric functions, EDAs in most cases cannot separate the RSPT terms from the exchange ones and have to be compared to $E^{(2)}_{\text{indx}}$ and $E^{(2)}_{\text{dispx}}$.

E. Asymptotic expansion of interaction energy

The asymptotic form of the interaction energy results from application of the multipole expansion of V in the expressions for the electrostatic, induction, and dispersion energies. For the electron repulsion term, this expansion, valid when the distance between monomers becomes large, can be written as

$$\frac{1}{r_{12}} = \sum_{l_A,l_B=0}^{\infty} \sum_{m=-l_<}^{l_<} K^m_{l_A l_B}\, Q^m_{l_A}(\boldsymbol{r}_1)\, Q^{-m}_{l_B}(\boldsymbol{r}_2)\, R^{-l_A-l_B-1} \tag{53}$$

where $l_< = \min(l_A, l_B)$, $K^m_{l_A l_B}$ is a combinatorial coefficient

$$K^m_{l_A l_B} = (-1)^{l_B} \frac{(l_A + l_B)!}{[(l_A+m)!\,(l_A-m)!\,(l_B+m)!\,(l_B-m)!]^{1/2}} \tag{54}$$

and $Q^m_l(\boldsymbol{r})$ are the solid harmonics (spherical 2^lth-pole moment operators) defined in terms of the standard spherical harmonics as

$$Q^m_l(\boldsymbol{r}) = -\left(\frac{4\pi}{2l+1}\right)^{1/2} r^l Y^m_l(\hat{\boldsymbol{r}}). \tag{55}$$

Applying the expansion of Eq. (53) to evaluate expression (13) for the electrostatic energy we get

$$E^{(1)}_{\text{elst}} = \sum_{l_A,l_B=0}^{\infty} \sum_{m=-l_<}^{l_<} K^m_{l_A l_B}\, R^{-l_A-l_B-1} \int \rho^{\text{tot}}_A(\boldsymbol{r}_1) Q^m_{l_A}(\boldsymbol{r}_1)\, d^3\boldsymbol{r}_1 \int \rho^{\text{tot}}_B(\boldsymbol{r}_2) Q^{-m}_{l_B}(\boldsymbol{r}_2) d^3\boldsymbol{r}_2. \tag{56}$$

The first (second) of the two integrals can be recognized as the mth ($-m$th) spherical component of the multipole moment of monomer A (B) of rank l_A (l_B). Thus, the terms of this expansion represent interactions of permanent multipoles on molecule A with those on B. If the molecules are neutral and polar, the first nonvanishing moment is the dipole moment. For such systems, the electrostatic energy decays as $1/R^3$. In general, the leading decay is $R^{-l_A-l_B-1}$ if the lowest multipole moments of monomers are l_A and l_B. This gives the well-known interpretation of the electrostatic energy in terms of dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, … Coulomb interactions. The multipole series can represent well the electrostatic energy at large separations despite the fact that it is divergent at any R because of the neglect of the charge-penetration effects. This expansion is, however, asymptotically convergent, i.e., a properly truncated expansion is arbitrarily close to the electrostatic energy if R is large enough. These charge-penetration effects can be included if $1/r_{12}$ is expanded in using the bipolar expansion[53]. One can obtain then appropriate charge-overlap corrections that dampen the divergence of the individual multipole interaction terms.

Similar derivations can be performed for the induction and dispersion energies. In the second order, the asymptotic expansion depends also on monomers' polarizabilities: static in the case of induction energy and dynamic in the case of dispersion energy. The leading term in the expansion of the induction energy is R^{-2l-4}, where l is the smallest rank among the nonzero multipole moments (including the monopole) of the two interacting monomers (e.g, R^{-6} for the water dimer and R^{-10} for the methane dimer). This is because the induced multipoles are proportional to the polarizabilites of monomers and therefore they always start from the dipole, but their interaction with permanent multipoles depends on the lowest nonvanishing permanent moment. We see that for neutral nonpolar systems the induction interaction energy should be less important than the dispersion interaction since the latter always decays as R^{-6}. The third-order induction energies decay as R^{-6} for ionic and R^{-9} for neutral dimers, unless at least one of the monomers has a symmetry which results in a faster decay. For the interaction of two spherically symmetric atoms, the third-order dispersion energy decays[30] as R^{-11}.

Since the asymptotic expansion is derived from the RSPT components of SAPT and the exchange and overlap effects are negligible in the asymptotic region, SAPT interaction energies are seamlessly connected to the asymptotic expansion in the sense that the agreement between the two interaction energies becomes arbitrarily close for R sufficiently large. In practice, 2-3 digit agreement is reached already at R about 2-3 times larger than the van der Waals minimum distance.

IV. SAPT CONTRIBUTIONS AND EDA METHODS

The relations discussed in Sec. III clearly show that each SAPT contribution is uniquely determined, with a well-defined complete basis set limit. Furthermore, these contributions have a clear physical interpretation and their sum is a good approximation of the total interaction energy. The conclusion regarding EDA methods is that their goal should be to partition supermolecular interaction energy in such a way that each component resulting from an EDA is in one-to-one correspondence with a SAPT contribution both in terms of numerical values and in terms of physical interpretation. This is indeed the case for a number of EDA methods.

One point of distinction are charge-delocalization (also called charge-transfer) energies. This physical effect is present in $E^{(2)}_{\mathrm{indx}}$ and in $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$, yet SAPT gives no unique means of extracting charge delocalization effects from the overall induction effects. However, one may ask if it even makes sense to distinguish the energetic effect of charge delocalization. The perturbation of each monomer leads to a deformation of its electron charge distribution. One can trivially obtain the difference $\Delta\rho_{AB} = \rho_{AB} - \rho_A - \rho_B$. However, this differential density just spreads over the whole space and represents only the charge deformation relative to the sum of monomer densities. One cannot uniquely determine the total charge transferred from monomer A to monomer B since this requires choosing an arbitrary boundary between the monomers. Thus, since even the spatial charge delocalization is not a well-defined quantity, the energetic effect of this delocalization has to be still harder to determine. Part of the problem is also the smallness of this effect: for majority of dimers bound by noncovalent interactions, even if some surface separating monomers is chosen, reasonable choices lead to transfers of only a small fraction of electron charge between monomers. This is in contrast with molecular charge-transfer transitions due to absorption of light, when the amount of charge transferred can be about one electron.

Another question is that even assuming the charge-delocalization energy can be determined, what would be the use of such information besides getting a physical insight? The physical insight is, obviously, very important, but one would like to have some use of this quantity that could help to predict properties of interacting systems. One might think that this term could be separately fitted in force fields, but none of major biomolecular force fields include such terms, nor are they used in force fields fitted to *ab initio* interaction energies[59,123,138–141]. Note that the functional forms of the latter force fields are able to fit interaction energies with uncertainties lower than the uncertainties of the computed interaction energies.

Despite of the comments made above, most EDA methods include charge-delocalization energies. As long as the sum of the charge-delocalization energy and what is usually called polarization energy is close to $E^{(2)}_{\rm indx} + \delta E^{\rm HF}_{\rm int,resp}$, any such splitting can be deemed acceptable.

One should point out that methods have been proposed for determining charge-delocalization energy within SAPT. The first method, proposed by Stone and Misquitta[142], achieves a decomposition using some specific locations of basis functions. In SAPT, there are two basis sets used, one per monomer. A given monomer basis set can be located only on this monomer or also on the interacting partner[129]. If the latter functions are not present, i.e., in a monomer-centered basis set (MCBS), the induction energy converges very slowly at short range[129] and one may assume that this is due to difficulties such a basis set encounters in modelling charge delocalization. Thus, the charge-delocalization energy can be defined as the difference between the induction energies computed using a dimer-centered basis set (DCBS) and MCBS. The problem with this method is that if an MCBS approaches completeness, the induction energy does approach the exact value and the charge-delocalization effect becomes very small. Another method proposed by Misquitta[143] is based on a regularization of V introduced in Ref. 88. Such regularization consists of replacing infinite electron-nuclear attraction wells by finite ones. This reduces charge delocalization in the induction wave functions and leads to a reduced magnitude of the induction energies. The differences between non-regularized and regularized induction energies can be assumed to be a measure of the energetic effect of charge delocalization. However, the value of the regularization parameter has to be chosen arbitrarily and this does influence the results. More recently, Misquitta and Stone[140] proposed a model that uses the damped asymptotic expansion of induction energy to define the polarization component of the induction energy, while the difference between the total induction energy and this component defines the charge-delocalization energy. An important feature of this approach is that it can be extended to $\delta E^{\rm HF}_{\rm int,resp}$. A problem with this approach is that damping is nonunique and, as mentioned earlier, that there are terms in the induction energy that are not a part of the damped asymptotic expansion[53,79,80] (the so-called "spherical" terms). In the approach of Ref. 140, such terms contribute to the charge-delocalization energies, but it is not clear if this is an appropriate choice.

Table I. SAPT components of interaction energies of selected dimers as well as the total SAPT(DFT) and CCSD(T) interaction energies (Ref. 115 and unpublished results from that work). Intermolecular separations are in Å and energies are in kcal/mol. $\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$ is not included for dimers containing benzene.

dimer	R	$E^{(1)}_{\mathrm{elst}}$	$E^{(1)}_{\mathrm{exch}}$	$E^{(2)}_{\mathrm{indx}}$	$E^{(2)}_{\mathrm{dispx}}$	$\delta E^{\mathrm{HF}}_{\mathrm{int,resp}}$	total	CCSD(T)
water dimer	2.31	-30.1834	63.1796	-10.4850	-8.5641	-6.8250	7.1221	8.3579
	2.91	-8.1301	7.8782	-1.3816	-2.4053	-0.9403	-4.9791	-5.0051
	6.51	-0.3148	0.0000	-0.0032	-0.0104	-0.0001	-0.3285	-0.3225
ethanol dimer	3.256	-6.5661	14.0186	-0.8976	-7.2439	-1.0607	-1.7497	-1.2469
	3.558	-3.0535	5.4234	-0.4495	-4.4316	-0.3867	-2.8979	-2.7159
	6.558	-0.1129	0.0004	-0.0048	-0.0952	-0.0001	-0.2126	-0.2146
imidazole dimer	4.925	-26.9250	42.6896	-8.0881	-8.6006	-6.5760	-7.5001	-5.7778
	5.247	-14.9477	15.2506	-3.2864	-4.6927	-2.6027	-10.2789	-10.0238
	8.247	-1.2011	0.0009	-0.0441	-0.0850	-0.0017	-1.3310	-1.3334
benzene–water	2.5	-12.4001	30.3981	-2.4623	-9.9100		5.6257	5.4577
	3.0	-4.2862	6.8473	-0.7539	-4.4188		-2.6116	-2.6842
	6.0	-0.3322	0.0004	-0.0130	-0.0764		-0.4211	-0.3978
benzene–methane	3.28	-3.4974	9.9001	-0.3181	-5.5936		0.4910	0.1194
	3.8	-0.8884	2.2305	-0.1036	-2.5631		-1.3247	-1.4280
	5.8	-0.0386	0.0042	-0.0070	-0.1834		-0.2248	-0.2157

V. NUMERICAL EXAMPLES

Table I shows SAPT physical contributions to interaction energies of a selected set of dimers. More examples can be found in the SAPT papers cited earlier, as most of such papers include the components for a number of dimers' geometries. The data in Table I are from Ref. 115 inclusing unpublished results from that work. The details of the calculations and all dimers' geometries can be found in the Supplementary Information of that reference. For each dimer, the three consecutive values of R listed in Table I correspond to the repulsive, near-minimum, and the asymptotic regions of the radial interaction energy curves for the angular orientation corresponding to the van der Waals minimum of the dimer. The components listed can be used for comparisons with the components resulting from various EDAs. The total SAPT(DFT) energies in Table I are in good agreement withthe CCSD(T) interaction energies listed in the last column.

Appendix: Third-order induction energy

In contrast to the second-order case, separation of the induction energy in higher orders is not straightforward. A definition of the infinite-order induction energy was proposed in Ref. 53 (see also a more extensive discussion of this approach in Ref. 107). This definition leads to the formula for $E^{(3)}_{\rm ind}$ given by Eq. (60) in Ref. 107 [or equivalently by Eq. (20) in Ref. 53 where the reduced-resolvent notation is used]. In both cases, $E^{(3)}_{\rm ind}$ is expressed via the zeroth- and first-order functions only. To get an alternative physical interpretation of this quantity, we derive here an expression for $E^{(3)}_{\rm ind}$ involving only the second-order induction functions. The infinite-order induction energy can be defined[53] as the minimum of the expectation value of $H_0 + V$ with the trial function of the form $\tilde{\Psi}^A_{\rm ind}\tilde{\Psi}^B_{\rm ind}$

$$J_{\rm ind}\left[\tilde{\Psi}^A_{\rm ind}, \tilde{\Psi}^B_{\rm ind}\right] \equiv \frac{\langle\, \tilde{\Psi}^A_{\rm ind}\tilde{\Psi}^B_{\rm ind}|H_0 + V|\tilde{\Psi}^A_{\rm ind}\tilde{\Psi}^B_{\rm ind}\,\rangle}{\langle\, \tilde{\Psi}^A_{\rm ind}\tilde{\Psi}^B_{\rm ind}|\tilde{\Psi}^A_{\rm ind}\tilde{\Psi}^B_{\rm ind}\,\rangle}. \tag{A.1}$$

A simple way to derive the equations for the induction functions is to first assume that the exact induction wave function for monomer B is known. Equation (A.1) can then be written as

$$J_{\rm ind}\left[\tilde{\Psi}^A_{\rm ind}, \Psi^B_{\rm ind}\right] = \frac{\langle\, \tilde{\Psi}^A_{\rm ind}|H_A + \bar{\Omega}_B|\tilde{\Psi}^A_{\rm ind}\,\rangle}{\langle\, \tilde{\Psi}^A_{\rm ind}|\tilde{\Psi}^A_{\rm ind}\,\rangle}, \tag{A.2}$$

where

$$\bar{\Omega}_B = \frac{\langle\, \Psi^B_{\rm ind}|V\Psi^B_{\rm ind}\,\rangle + \langle\, \Psi^B_{\rm ind}|H_B|\Psi^B_{\rm ind}\,\rangle}{\langle\, \Psi^B_{\rm ind}|\Psi^B_{\rm ind}\,\rangle}. \tag{A.3}$$

The standard application of the variational principle leads then to the following equation for the induction wave function

$$\left[H_A + \bar{\Omega}_B\right]\Psi^A_{\rm ind} = \mathcal{E}\Psi^A_{\rm ind}, \tag{A.4}$$

where $\mathcal{E} = J_{\rm ind}[\Psi^A_{\rm ind}, \Psi^B_{\rm ind}]$. The analogous equation for monomer B is

$$\left[H_B + \bar{\Omega}_A\right]\Psi^B_{\rm ind} = \mathcal{E}\Psi^B_{\rm ind}. \tag{A.5}$$

If all quantities in Eqs. (A.4) and (A.5) are expanded in powers of V, one gets (using a self-explanatory short-hand notation)

$$\mathcal{E} = \mathcal{E}^0 + \mathcal{E}^1 + \mathcal{E}^2 + \mathcal{E}^3 + \cdots = E^A_0 + E^B_0 + E^{(1)}_{\rm elst} + E^{(2)}_{\rm ind} + E^{(3)}_{\rm ind} + \ldots, \tag{A.6}$$

$$|A\rangle = |A^0\rangle + |A^1\rangle + |A^2\rangle + \dots, \tag{A.7}$$

and similarly for monomer B, where all the terms in the sums except for the last ones have been defined before. To derive formulas for the latter quantities, we start from the following expansion of $\bar{\Omega}_B$:

$$\bar{\Omega}_B = \Omega_B^0 + \Omega_B^1 + \Omega_B^2 + \Omega_B^3 + \dots, \tag{A.8}$$

where

$$\Omega_B^0 = E_0^B; \quad \Omega_B^1 = \langle\, B^0|V|B^0\,\rangle = \Omega_B + \langle\, B^0|V^A|B^0\,\rangle + V_0; \tag{A.9}$$

$$\Omega_B^2 = 2\langle\, B^0|V|B^1\,\rangle - \langle\, B^0|\Omega_A|B^1\,\rangle \tag{A.10}$$

and

$$\Omega_B^3 = \langle\, B^1|V|B^1\,\rangle + 2\langle\, B^0|V|B^2\,\rangle - 2\langle\, B^0|\Omega_A|B^2\,\rangle - \langle\, B^0|V|B^0\,\rangle\langle\, B^1|B^1\,\rangle. \tag{A.11}$$

The second-order equation defining $|B^2\rangle$ is

$$(H_B - E_0^B)|B^2\rangle = \big(\langle\, B^0|\Omega_A|B^0\,\rangle - \Omega_A\big)\,|B^1\rangle + \big(\langle\, B^0|\Omega_A|B^1\,\rangle - 2\langle\, A^0|V|A^1\,\rangle\big)\,|B^0\rangle, \tag{A.12}$$

with an analogous equation for $|A^2\rangle$. Finally, the third-order equation is

$$(H_A - E_0^A)|A^3\rangle = \sum_{i=1}^{3} \left(\mathcal{E}^i - \Omega_B^i\right)|A^{3-i}\rangle, \tag{A.13}$$

resulting in the following expression for the third-order induction energy

$$\mathcal{E}^3 = \langle\, A^0|\Omega_B|A^2\,\rangle + 2\langle A^0B^0|V|A^1B^1\rangle + \langle\, B^1|\Omega_A|B^1\,\rangle - \langle\, B^0|\Omega_A|B^0\,\rangle\langle\, B^1|B^1\,\rangle. \tag{A.14}$$

Since

$$\langle\, B^1|\Omega_A|B^1\,\rangle = \langle\, B^0|\Omega_A|B^2\,\rangle + \langle\, B^0|\Omega_A|B^0\,\rangle\langle\, B^1|B^1\,\rangle - 2\langle A^0B^0|V|A^1B^1\rangle, \tag{A.15}$$

we finally obtain

$$E_{\text{ind}}^{(3)} \equiv \mathcal{E}^3 = \langle\, A^0|\Omega_B|A^2\,\rangle + \langle\, B^0|\Omega_A|B^2\,\rangle. \tag{A.16}$$

Returning to the explicit notation, Eq. (A.16) becomes

$$E_{\text{ind}}^{(3)} = \langle\Psi_0^A|\Omega_B|\Psi_{\text{ind}}^{(2)A}\rangle + \langle\Psi_0^B|\Omega_A|\Psi_{\text{ind}}^{(2)B}\rangle. \tag{A.17}$$

To to find an explicit expression for $\Psi_{\rm ind}^{(2)A}$, let us first write the equivalent of Eq. (A.12) for monomer A:

$$(H_A - E_0^A)|A^2\rangle = \left(\langle\, A^0|\Omega_B|A^0\,\rangle - \Omega_B\right)|A^1\rangle + \left(\langle\, A^0|\Omega_B|A^1\,\rangle - 2\langle\, B^0|V|B^1\,\rangle\right)|A^0\rangle, \quad \text{(A.18)}$$

which leads to the following formula for the second-order induction function of monomer A expressed as a spectral sum

$$\Psi_{\rm ind}^{(2)A} = \sum_{k\neq 0} \frac{\langle \Psi_k^A|\langle\Psi_0^A|\Omega_B\Psi_0^A\rangle - \Omega_B|\Psi_{\rm ind}^{(1)A}\rangle}{E_k^A - E_0^A}\Psi_k^A - 2\sum_{k\neq 0}\frac{\langle\Psi_k^A\Psi_0^B|V_{\rm ee}|\Psi_0^A\Psi_{\rm ind}^{(1)B}\rangle}{E_k^A - E_0^A}\Psi_k^A. \quad \text{(A.19)}$$

In practice, $E_{\rm ind}^{(3)}$ is much easier to compute using the expression depending only on the zeroth- and first-order functions, see Eq. (A.22) below, but the use of the second-order function allows a transparent interpretation of the third-order induction energy. Of course, the importance of this function stems also from the fact that it can be used to compute the fourth- and fifth-order induction energy contributions.

Expression (A.17) can be written in terms of densities as

$$E_{\rm ind}^{(3)} = \frac{1}{2}\int \rho_{\rm ind}^{(02)A}(\boldsymbol{r})\omega^B(\boldsymbol{r})d^3\boldsymbol{r} + \frac{1}{2}\int \rho_{\rm ind}^{(02)B}(\boldsymbol{r})\omega^A(\boldsymbol{r})d^3\boldsymbol{r} \quad \text{(A.20)}$$

where $\rho_{\rm ind}^{(02)A}(\boldsymbol{r})$, a component of the total second-order induction density $\rho_{\rm ind}^{(2)A}(\boldsymbol{r})$, is defined by a procedure similar to that leading to Eq. (21), but with $\Psi_{\rm ind}^{(2)A}$ added to Ψ^A

$$\begin{aligned}\rho_{\rm ind}^{(2)A}(\boldsymbol{r}) =& 2N_A \sum_{s,s_2,\ldots,s_N}\int \Psi_0^A(\boldsymbol{x},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_{N_A})\Psi_{\rm ind}^{(2)A}(\boldsymbol{x},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_{N_A})d^3\boldsymbol{r}_2\ldots d^3\boldsymbol{r}_{N_A}\\ &+ N_A\sum_{s,s_2,\ldots,s_N}\int \Psi_{\rm ind}^{(1)A}(\boldsymbol{x},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_{N_A})\Psi_{\rm ind}^{(1)A}(\boldsymbol{x},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_{N_A})d^3\boldsymbol{r}_2\ldots d^3\boldsymbol{r}_{N_A}\\ &= \rho_{\rm ind}^{(02)A}(\boldsymbol{r}) + \rho_{\rm ind}^{(11)A}(\boldsymbol{r}), \end{aligned} \quad \text{(A.21)}$$

with the second-order induction function given by Eq. (A.19) and the two terms in the last expression corresponding to the consecutive terms in the preceding expression. Thus, the second-order induction densities have two components: one originating from the second-order induction function and one originating from the product of first-order induction functions, and only the former term enters the expression for $E_{\rm ind}^{(3)}$. Equation (A.20) shows that the third-order induction interaction can be interpreted as the interaction of the second-order induction density components resulting from $\Psi_{\rm ind}^{(2)X}$ with the unperturbed electrostatic potentials. Note again the factors of 1/2 multiplying the Coulomb interactions of $\rho^{(02)A}_{\text{ind}}(\boldsymbol{r})$ with $\omega^B(\boldsymbol{r})$ in the first term, and analogously in the second.

Using Eq. (A.15), formula (A.16), expressed in terms of the unperturbed functions and of the second-order induction functions, can be transformed into formula (60) from Ref. 107 expressed in terms of the unperturbed functions and of the first-order induction functions only:

$$\begin{aligned} E^{(3)}_{\text{ind}} &= \langle\, A^1|\Omega_B|A^1\,\rangle + \langle\, B^1|\Omega_A|B^1\,\rangle - \langle\, A^0|\Omega_B|A^0\,\rangle\langle\, A^1|A^1\,\rangle - \langle\, B^0|\Omega_A|B^0\,\rangle\langle\, B^1|B^1\,\rangle \\ &\quad + 4\langle A^0B^0|V|A^1B^1\rangle, \end{aligned} \tag{A.22}$$

which written in explicit notation is the same as Eq. (60) in Ref. 107. This formula can be expressed in terms of densities as

$$E^{(3)}_{\text{ind}} = \int \rho^{(11)A}_{\text{ind}}(\boldsymbol{r})\tilde{\omega}^B(\boldsymbol{r})d^3\boldsymbol{r} + \int \rho^{(11)B}_{\text{ind}}(\boldsymbol{r})\tilde{\omega}^A(\boldsymbol{r})d^3\boldsymbol{r} + \iint \rho^{(1)A}_{\text{ind}}(\boldsymbol{r}_1)\frac{1}{r_{12}}\rho^{(1)B}_{\text{ind}}(\boldsymbol{r}_2)d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2, \tag{A.23}$$

where

$$\tilde{\omega}^B(\boldsymbol{r}) = \omega^B(\boldsymbol{r}) - \frac{1}{N_A}\int \rho^A_0(\boldsymbol{r})\omega^B(\boldsymbol{r})d^3\boldsymbol{r}.$$

The third term is the same as in Eq. (25). The first term is numerically the same as the first term in Eq. (25), but the density is now the component of the second-order induction density resulting from the product of the first-order induction functions and it interacts with the shifted electric potential of molecule B, similarly for the second term.

One more interpretation of $E^{(3)}_{\text{ind}}$ can be obtained via regrouping the terms in formula (A.17) and defining an alternative second-order induction function, different from the one of Eq. (A.19). The resulting expression for the third-order induction energy is algorithmically different from Eq. (A.17), but gives the same numerical value of this quantity. The former definition just neglects the second expression on the right hand side of Eq. (A.19)

$$\bar{\Psi}^{(2)A}_{\text{ind}} = \sum_{k\neq 0} \frac{\langle \Psi^A_k|\langle\Psi^A_0|\Omega^B\Psi^A_0\rangle - \Omega^B|\Psi^{(1)A}_{\text{ind}}\rangle}{E^A_k - E^A_0}\Psi^A_k. \tag{A.24}$$

The alternative second-order equation is

$$(H_A - E^A_0)|\bar{A}^2\rangle = \big(\langle\, A^0|\Omega_B|A^0\,\rangle - \Omega_B\big)\,|A^1\rangle. \tag{A.25}$$

Notice that $|\bar{A}^2\rangle$ cannot be called the second-order *induction* function since the function of Eq. (A.18) is the unique and only such function. We can now design an energy expression

$$E^{(3)}_{\mathrm{ind}} = \langle\, A^0|\Omega_B|\bar{A}^2\,\rangle + \langle\, B^0|\Omega_A|\bar{B}^2\,\rangle + 4\langle A^0B^0|V|A^1B^1\rangle \tag{A.26}$$

or in explicit notation

$$E^{(3)}_{\mathrm{ind}} = \langle\Psi^A_0|\Omega_B|\bar{\Psi}^{(2)A}_{\mathrm{ind}}\rangle + \langle\Psi^B_0|\Omega_A|\bar{\Psi}^{(2)B}_{\mathrm{ind}}\rangle + 4\langle\Psi^A_0\Psi^B_0|V|\Psi^{(1)A}_{\mathrm{ind}}\Psi^{(1)B}_{\mathrm{ind}}\rangle, \tag{A.27}$$

which produces the same numerical values as given by Eq. (A.17). To show this, transform Eq. (A.26) into Eq. (A.22). To this end, write Eq. (A.25) as

$$|\bar{A}^2\rangle = R^A_0\left(\langle\, A^0|\Omega_B|A^0\,\rangle - \Omega_B\right)|A^1\rangle, \tag{A.28}$$

where R^A_0 is the reduced resolvent of monomer A, and use it in Eq. (A.26). We get

$$\langle\, A^0|\Omega_B|\bar{A}^2\,\rangle = \langle A^0|\Omega_B R^A_0\left(\langle\, A^0|\Omega_B|A^0\,\rangle - \Omega_B\right)|A^1\rangle = \langle\, A^1|\Omega_B|A^1\,\rangle - \langle\, A^0|\Omega_B|A^0\,\rangle\langle\, A^1|A^1\,\rangle \tag{A.29}$$

and similarly for the second term, which indeed gives the desired formula. Equation (A.27) expressed in terms of densities yields Eq. (25).

Appendix: Conversations

Mo *et al.* commented:

The authors focus on the elegance of the SRS formulation of SAPT, but perhaps ignore chemistry, and at the same time they are dismissing all other EDA methods as nonunique. They make statements about the uniqueness and precision of SAPT in providing energy partition that sums to the total interaction energy between the molecules/fragments A and B, and dismisses effects like charge-transfer, covalency, charge delocalization, etc. which arise from other EDA methods (and also from NBO, VB and BLW). Our general comment is that there are multiple perspectives in a matter of fact, which are in no way unphysical. What is unscientific is to claim uniqueness and truth for one of these choices, namely SAPT, and to dismiss on this ground all other approaches. This is done without providing the reader with a single example that compares SAPT (e.g., what about BrHBr$^-$?) to other EDA methods. In a nutshell the paper is a blizzard of equations without any example. This is a major problem for most chemists, who would like to see examples with numerical data, as proofs of correctness of statements.

Reply:

We do not believe we ignore chemistry, but it depends what one has in mind by “chemistry”. Noncovalent intermolecular interactions are a part of chemistry and our whole paper is devoted to such interactions. Thus, in this sense we cannot agree that we ignore chemistry. On the other hand, we do not discuss making and breaking of chemical bonds since these are not processes that SAPT was designed for (although please see a discussion of this issue later on). In fact, the first sentence in the abstract states “Symmetry-adapted perturbation theory (SAPT) is a method for computational studies of noncovalent interactions between molecules.”

We also do not believe we are dismissing all other EDA methods as nonunique. While this is a plain fact that the EDA methods are highly nonunique, the physical components in some of these methods come reasonably close to the corresponding SAPT components. Such methods are, in our opinion, important since their application on top of some supermolecular calculations of interaction energies does give sufficiently precise physical insights.

Concerning the dismissal of “effects like charge-transfer, covalency, charge delocalization”. Indeed, SAPT is not designed to investigate covalency effects as it is practically limited to noncovalent interactions. We make no statements on EDA methods applied to chemically reactive systems. One the other hand, we do not dismiss charge-delocalization effects (which in our terminology are equivalent to charge-transfer effects) and we discuss these effects in Sec. IV. To summarize this discussion: SAPT does include charge-delocalization effects, but it appears there is no unique ways to separate them. However, very reasonable ways to perform such separation approximately have been designed by Misquitta and Stone[140,142,143] and analyzed from the point of view of applications in developments of force fields[77].

While we agree that different viewpoints are useful in science, it does not mean that all viewpoints are correct. In particular, if method X states that the dispersion interaction in a given dimer is zero, while method Y states that it is one of major attractive forces, only one of these viewpoints can be correct. Thus, if the authors of method X believe their results is correct, they should explain why method Y makes wrong predictions.

There are so many examples of SAPT interaction energy decompositions in literature that we did not think examples are needed in the present paper. Nevertheless, in the revised version we added Table I with such examples. The geometries of the dimers included are available in literature, so these data can perhaps serve as a useful reference point for authors of EDA approaches. We have not included the $BrHBr^-$ dimer Table I. While one can trivially compute SAPT components for this system, it is a system which is to a large effect covalently bound, see the recent work on FHF^- dimer[144]. While both systems would be interesting cases to study by SAPT, their special character does not make them appropriate as examples on SAPT analysis of noncovalent interactions. One may add that a somewhat similar system, H_2O-F^-, is included in Ref. 77.

Most published SAPT calculations listed the components of interaction energies, at least for some selected geometries. Here is a selection of such papers for readers who would like to study more examples: water dimer (Refs. 20, 22, 145, and 146), helium dimer (Refs. 21 and 147), water-uracil (Ref. 148), He-F^- (Ref. 149), Ar–H_2 (Ref. 150), Ar–HF (Ref. 84), He-H_2O (Ref. 151), water trimer (Ref. 152), and many other.

Mo *et al.* commented:

On page 15 the authors state that "one cannot define uniquely the charge transferred from one monomer". But the fact is that charge transfer accompanies nevertheless many reactions. How does SAPT handles the CT in e.g., S_N2 reaction? As the author says, CT is handled as damping of other terms of SAPT. It is hard to buy such a statement.

Reply:

We never say that there is no charge delocalization (or transfer) in noncovalent intermolecular interactions, we only say that the amount of charge that was delocalized cannot be uniquely determined. These are two different statements. Again, we make no statements about chemical reactions.

We never say that charge delocalization energy is due to damping of asymptotic expansion. We just point out that in the method of determining this energy developed by Misquitta and Stone in Ref. 140, the numerical value of this quantity depends on assumptions concerning damping.

Mo *et al.* commented:

At the end of page 15, the authors speak about CT and ask: "what would be the use of such information besides a physical insight?" Let us ask the author: is there any science without insight?

Reply:

We were not trying to belittle the importance of physical insight, but the major goal of science are predictions about nature. We added an additional sentence at this place to make our views clear.

Mo *et al.* commented:

On page 16, the authors do recognize charge transfer-delocalization "and one may assume that this is due to the difficulties of such a basis set to model charge delocalization". It is good that Stone found a way to add CT to SAPT. There is not much chemistry without CT.

Reply:

We recognize the existence of charge delocalization all the time. In the sentence quoted, we discuss the assumptions of the method proposed by Stone and Misquitta[142] in 2009 and this sentence is not a statement of recognition of charge delocalization. The work of these authors shows how difficult it is to define charge delocalization energies within SAPT as the three proposed approaches[140,142,143] produce quite different numerical values of these quantities. This is one more confirmation of the point we make: charge delocalization is a fact, a unique determination of its energetic effect is not possible, but reasonable approximate definitions of this effect may be useful.

Mo *et al.* commented:

In fact, MO (or MO-CI – any level) theory tells us that when two molecules approach, there are orbital interactions dominated by one HOMO in one side and one LUMO on the other side. These orbital interactions stabilize the complex by CT interaction that creates covalency. Where is this in SAPT?

Reply:

Again, SAPT is not designed to treat covalent bonds.

Mo *et al.* commented:

In addition, when two molecules approach one another, their individual molecular orbitals will be perturbed and thus reshuffled. This physical effect is the polarization effect. Thus, the obvious question would be how the SAPT method quantifies the electron (or charge) transfer and polarization energies. The author did address this question in passing in the end of the paper by mentioning the approaches by Stone and Misquitta.

Reply:

The polarization effect, which we call the induction effect, is discussed in detail in Sec. III B.

We can only repeat one more time that a unique separation of induction energies into parts due to “fixed” (but deformed) and delocalized charge is not possible. Nonunique, approximate separations such as those proposed by Misquitta and Stone[140,142,143] can be useful.

Mo *et al.* commented:

In chemistry, not only inter- but also intramolecule charge transfer plays a significant role and has been well recognized. For example, in benzene (C_6H_6), the delocalization of the six p electrons has a profound influence on molecular structures and properties. It will be helpful for readers if some data from the SAPT computations in this regard can be presented.

Reply:

In SAPT, monomers can be described at various levels of theory, see Sec. II. Even the lowest possible level, the HF method, should take account of these effects. This is demonstrated by the fact that the SAPT potential for the benzene dimer[153] is the most accurate published one for this system, capable to produce predictions of spectroscopic accuracy[154].

Mo *et al.* commented:

We are also curious about the basis set dependency of the SAPT method. Taking the simple example of a two-body complex $H_3N\cdots BH_3$, can the author show the SAPT results with the basis sets from 6-31G to 6-311+G(d) to 6-311++G(d,p) to aug-cc-pvtz for this very simple complex? Of course, the comparison of different correlated methods would also be helpful. We believe that the case of $H_3N\cdots BH_3$ with various basis sets would be illuminating if the author is willing to share the computation results.

Reply:

Multiple basis set convergence studies for SAPT components including the basis sets listed above and several other basis sets have been published, see in particular Refs. 22 and 129. We believe no further studies of basis set convergence are needed.

Mo *et al.* commented:

Getting back to the Introduction, the author wrote that “there is no place for terms not present in SAPT since SAPT’s contributions sum up to an accurate value of the interaction energy”. This is quite confusing as all other EDA approaches also sum up all terms to an accurate value of the interaction energy. We do not see disagreements with the interaction energy values, and all controversies come from the interpretation of the energy terms. The accuracy of the SAPT towards the final interaction energies cannot be used as evidence for the correctness of its physical interpretations or energy partition schemes. Again, data can speak better.

Reply:

This statement means the following: virtually all EDA methods identify terms labeled in the same way as in SAPT: electrostatic, first-order exchange, induction, and dispersion energies. In SAPT, these terms sum up to an accurate total interaction energies. Thus, if these four components are defined in an EDA in such a way that they are close to the SAPT values, they also sum up to total interaction energies. Then, no other terms with significant magnitude can be added. We have modified the quoted text to make our point more clear.

Mo *et al.* commented:

Besides, any theoretical results need be justified by experimental evidence, directly or indirectly. In Section II, the author wrote "In fact, there is no resemblance between SAPT(DFT) and supermolecular DFT interaction energies for majority of dimers". This is again quite confusing. DFT interaction energies rely on the DFT methods themselves not any particular EDA method. It seems that the author is comparing orange with apple here as SAPT(DFT) and DFT are not at the same theoretical levels.

Reply:

SAPT results are fully confirmed by experimental evidence. The most convincing confirmation are vibration-rotation-tunneling (VRT) spectra of dimers and trimers: spectra computed from SAPT potentials agree very well with experiment[84,154–157]. Another example are crystal-structure predictions from SAPT-based force fields, which correctly identify the experimental crystal as one of the top-ranked polymorphs[158–163].

A different question is if the individual energy components predicted by SAPT can be related to experimental data. The evidence is less direct here, but it does exist. In the long-range region, the interaction energy of a dimer made from polar monomers is dominated by the electrostatic energy. For such systems, scattering experiments can sometimes identify the so-called long-range entrance-channel states which are located in the regions of strongest electrostatic interactions. Furthermore, the electrostatic energies are guiding crystallographers in designing crystals of polar molecules. The induction energy dominates the long-range total potential in interactions of ions with rare-gas atoms. Therefore scattering experiments on such systems directly probe the induction components of PESs. Similarly, interactions of rare-gas atoms are dominated at long range by the dispersion energies. Thus, the measured s-wave scattering lengths probe dispersion interactions. Finally, the exchange component is related to van der Waals radii of elements. This component determines the repulsive wall of potentials and the repulsive wall in turn determines the van der Waals radii.

The second question is orthogonal to the first. Yes, SAPT(DFT) and supermolecular DFT are different levels of theory. Still, different approaches can produce similarly accurate interaction energies. For example, interaction energies from high-order SAPT based on the FCI description of monomers agree to several digits with supermolecular FCI energies[16,18,66,127]. On the other hand, while SAPT(DFT) gives accurate interaction energies, those from supermolecular DFT, as it is well known, have in general dramatically large errors, mainly due to the fact that semilocal DFT methods do not reproduce dispersion energies at physically relevant intermolecular separations[118,164]. The underlying reason for this problem is the "shortsightedness" of interelectron interactions in semilocal DFT approximations. However, DFT describes monomers reasonably well. This is why Kohn-Sham monomer determinants and TD-DFT monomer density-density response functions can be used to construct SAPT(DFT) components. The dispersion energy is obtained in SAPT(DFT) from wave-function-type expressions and therefore the DFT shortsightedness problem does not matter. References 26 and 113 provide theoretical justifications for high accuracy of SAPT(DFT). It is easy to understand this in the case of electrostatic energy. Most variants of semilocal generalized-gradient approximation (GGA) DFTs give quite accurate electron densities, except at large separations from nuclei. Because of the latter problem, the first SAPT(KS) calculations[109] gave poor electrostatic energies. This problem can be fixed by applying the asymptotic correction as done in Refs. 110 and 111, leading to densities accurate at all separations. Since the electrostatic energy is just an integral of electron densities of unperturbed monomers, if the densities are accurate, so is the electrostatic energy.

Mo *et al.* commented:

On Page 4 the author states that SAPT in higher order is accurate even for diatomics, e.g., LiH. Can he show an example or two? There is no chemistry without delocalization, there is no chemistry without covalency. What about H_2? Where is the covalency in SAPT? What about resonance?

Reply:

The question presumably concerns chemically bound diatomics (for NCIs in diatomics, SAPT is accurate already in the low order). For two diatomics, H_2 and LiH, SAPT was applied to chemically bonded ground states of these systems[15,16,18,54,87,165]. Table I in Ref. 15 shows that in 60th order SRS recovers the energy of the singlet state of H_2 at $R = 2.0$ bohr to within 0.0005%. Table III in Ref. 18 shows there the best working variant of SAPT recovers the LiH binding energy at the chemical minimum to within 0.0001%. Figure 8 in the same paper shows potential energy curves in the region of chemical minimum computed using 4th-order SAPT. So clearly, SAPT can recover covalent interactions. Yet, because of the necessity to apply a high-order treatment, we do not recommend SAPT to study strong covalent interactions. However, this excellent convergence says nothing about presence or absence of charge delocalization. As already stated several times, SAPT does account for delocalization effects, but cannot separate them from polarization effects. Finally, resonances do appear in intermolecular interactions when the interacting systems are degenerate. It is possible to construct SAPT applicable to such systems[11].

Mo *et al.* commented:

Some technical questions:

Are the orbitals in A and B orthogonal? Presumably they are not since Pauli repulsion is accounted for during the anti-symmetrization procedure. But Pauli repulsion necessarily bring about electronic effects like CT. Where are these in the SAPT picture? Any example?

Reply:

Orbitals within system A are orthogonal to each other, and similarly for systems B. However, orbitals of A are not orthogonal to orbitals of B. This is independent of antisymmetrization as such non-orthogonality exists already at the level of RSPT. The non-orthogonality is treated in SAPT exactly, i.e., proper orbital overlap integrals appear in all formulas. Indeed, antisymmetrization leads to a distortion of charge density, so the exchange components of SAPT do contain some delocalization, it is not only the induction energy which contributes to charge delocalization. Since delocalization effects are not separable from charge distortion effects that do not involve any shift of charge, no examples can be given.

Mo *et al.* commented:

Doesn't SAPT miss one electronic effect like CT because its perturbation Hamiltonian includes only bielectronic Coulombic terms $[H_0 = H_A + H_B + H_C + V_{AB} + V_{AC} + V_{BC} + \ldots]$?

Reply:

The terms on the right-hand side define the exact Hamiltonian of Schrödinger's quantum mechanics for atoms and molecules. No three-electrons interactions are present in such

Hamiltonians. [BTW, since this is the total Hamiltonian of a cluster, it should be denoted as H rather than H_0 since in the customary notation $H_0 = H_A + H_B + H_C$.]

Brink and Borrfors commented:

It is very reassuring that SAPT to high orders is formally an exact theory and can handle covalent bond formation. However, the most common SAPT variants are truncated at second order or possibly third order and better suited for weaker interactions. In addition, there are other approximations that commonly are employed, such as $\delta E^{\rm HF}_{\rm int,resp}$ (eq. 7) and the S^2 approximation. Is there any approach for estimating the accuracy of the employed SAPT level for a given problem? Can the $\delta E^{\rm HF}_{\rm int,resp}$ value be used as such an indicator? For example, does a value lower than a certain number or lower than a certain fraction of the total SAPT energy indicate that the SAPT level is sufficiently accurate for the problem at hand?

Reply:

As discussed above, SAPT is not designed for interaction leading to formation of covalent bonds. For NCIs, second-order treatment works well in practice. In fact, in most SAPT calculations basis set incompleteness errors are larger than SAPT theory errors. In a number of papers, SAPT interaction energies were compared to CCSD(T) energies at complete basis set (CBS) limit. Perhaps the most thorough comparison was performed in Ref. 115 on 10 dimers and about 100 configurations total. The median unsigned percentage error computed for all dimers in an augmented triple-zeta basis relative to CCSD(T)/CBS was 2.6%. This should be compared to the same error for CCSD(T) in the same basis set amounting to 1.2%.

Estimates of SAPT accuracy by comparisons to other accurate methods are the only reliable ones. The magnitude of $\delta E^{\rm HF}_{\rm int,resp}$ is not an indication of the overall error of SAPT. In fact, SAPT performs very well for interactions of strongly polar systems, while $\delta E^{\rm HF}_{\rm int,resp}$ is always large for such systems. Thus, other than the average errors such as those found in Ref. 115, there are no a priori estimates of the size of SAPT error for a given dimer. In practice, one usually performs CCSD(T) calculation for a couple of points on a potential energy surface to estimates the uncertainties of SAPT, as well as performs a few calculations at the CBS limits to estimate basis set incompleteness errors.

It appears that the errors due to the use of the S^2 approximation and due to the addition of $\delta E^{\rm HF}_{\rm int,resp}$ are smaller than the errors due to the truncation of SAPT expansion at the second order, although there is no study showing this unequivocally. The S^2 approximation can now be eliminated[124–126], however, it affects the results significantly only at very short separations and the S^2 errors are mostly removed by the use of $\delta E^{\rm HF}_{\rm int,resp}$. The physical reason for including $\delta E^{\rm HF}_{\rm int,resp}$ is to account for the induction and exchange-induction effects of the third (or fourth) and higher orders. For polar systems, the advantages of adding the third and higher-order induction effects much outweigh the small inaccuracies that this addition introduces in the first and second order.

Brink and Borrfors commented:

What are the main reasons for the higher accuracy of SAPT(DFT) compared to supermolecular DFT? Is the difference in interaction energy dominated by the more accurate description of the dispersion energy in the former approach or is SAPT(DFT) able to describe other energy contributions more accurately, as well? Is it still possible to determine third order and higher terms by a similar equation to eq. 7 ($\delta E^{\rm HF}_{\rm int,resp}$ approximation) in SAPT(DFT)? A related question concerns the functional dependence of SAPT(DFT). Is SAPT(DFT) less dependent than supermolecular DFT on the choice of DFT functional? Furthermore, which energy term in SAPT is most functional dependent?

Reply:

The reasons that SAPT(DFT) interaction energies are more accurate than the supermolecular DFT ones have already been discussed in the reply to one of the Mo *et al.* questions. Indeed, the inability of semilocal GGA approaches to recover dispersion interactions is one of the reasons. However, it is not the only reason. An extensive discussion[118] of the other reasons based on analysis of numerical results for several dimers led to the conclusion that inaccuracies originating from DFT components unrelated to the dispersion energy are of similar magnitude. This work analyzed the quantity

$$E^{\rm extra}_{\rm int} = E^{\rm DFT}_{\rm int} - E^{\rm dispersionless}_{\rm int},$$

where $E^{\rm DFT}_{\rm int}$ is the supermolecular DFT interaction energy and $E^{\rm dispersionless}_{\rm int}$ is a near-exact interaction energy minus the dispersion and exchange-dispersion contribution. If the dispersion energy was the only problem of DFT, it should recover $E^{\rm dispersionless}_{\rm int}$ well, i.e., $E^{\rm extra}_{\rm int}$ should be small (except possibly at very small intermonomer separations where the electrons of the interacting monomers get into the “visibility” region of DFT). Figures 4 and 6 in Ref. 118 show that this is not the case, in fact, the recovery of $E^{\rm dispersionless}_{\rm int}$ is poor. So the answer is confirmative: the accurate description of the dispersion interaction in SAPT(DFT) compared to essentially no description in supermolecular DFT is one reason for SAPT(DFT) being so much more accurate, but SAPT(DFT)'s ability to describe the other interaction energy contributions more accurately than does supermolecular DFT is another, perhaps equally important reason.

Yes, the addition of $\delta E^{\rm HF}_{\rm int,resp}$ is as rigorous in SAPT(DFT) as in SAPT based on wave-function description of monomers. The reason is that the orders in V in each version of SAPT are rigorously separated from each other. In particular, SAPT(DFT) in its current version includes only first- and second-order terms, while $\delta E^{\rm HF}_{\rm int,resp}$ includes only the third- and higher-order terms (plus a small "contamination" in lower orders which it the reason the addition of $\delta E^{\rm HF}_{\rm int,resp}$ is an approximation, as discussed above).

Yes, SAPT(DFT) interaction energies change insignificantly when different variants of GGAs are used (provided an asymptotic correction is applied) compared to dramatically different interaction energies from different variants of supermolecular DFT. This issue was investigate in a number of papers[26,113,166–169]. Interestingly, the PBE0 functional[170,171] shows consistently the best performance in SAPT(DFT) calculations.

The SAPT component most dependent on the choice of the density functional depends on type of interactions. For dispersion-bonded systems like rare-gas dimers, the effect is the largest in absolute terms for the dispersion energies, see for example Table IV in Ref. 26. For dimers of polar monomers, the largest effects come from the first-order and induction energies, see Table V in Ref. 26 and Table IV in Ref. 113.

Brink and Borrfors commented:

A limitation of SAPT for the analysis of larger systems seems to be the lack of an efficient procedure for structure optimization of molecular complexes. In particular, strong interactions often lead to conformational changes and changes to intramolecular geometry parameters, e.g. intramolecular bond lengths. How are the structure optimizations of such systems best handled? When employing SAPT(DFT) it does not seem advisable to use a supramolecular approach for structure optimization as supermolecular DFT is much less accurate than SAPT(DFT) for intermolecular interactions. Would it be possible to use a mixed approach where supermolecular calculations are used to determine binding conformations and intramolecular parameters and where SAPT is used for refining intermolecular distances? Would such a procedure be sufficiently accurate and can it be automated? A related question concerns the best approach for computing vibrational corrections (zero point and thermal corrections) to complexation enthalpies and free energies?

Reply:

Actually, our programs provide one of the most efficient approaches to structure optimization for molecular complexes. Let us focus first on rigid monomers. In this case, one needs monomers' structures. To get them, one can use standard electronic structure programs. For not too large monomers (containing up to couple dozen atoms), one can usually determine a small number of starting monomer's configurations based on chemical intuition. Then, local optimization algorithms (i.e., algorithms finding the minimum closest from the starting point) will reliably find global and local minima (conformers) of each monomer. If one wanted to proceed in this way to find minimum structures of the dimer, this approach would frequently fail since the locations of minima on the potential energy surface of the dimer are often in very nonintuitive places. Thus, many starting points would have to be tried, which makes such optimizations very expensive even at the DFT level. Our approach is to first fit a potential energy surface and then use the fit function to search for minima. Both tasks are performed completely automatically by the autoPES programs[123,141]. This protocol is the mixed approach mentioned in the question (and yes, the procedure is accurate, robust, and fully automated). For optimization of monomer geometries any method can be used, e.g., MP2, not necessarily DFT (and if DFT is used, it should be a dispersion-corrected DFT approach). Since the latest version of autoPES can develop flexible-monomer potential energy surfaces, one can now optimize full-dimensional dimer structures. This allows investigations of effects of intermolecular interactions on monomer conformations.

As mentioned earlier, SAPT potentials for smaller clusters have been often used to compute VRT spectra of these clusters. Such calculations produce very accurate zero-point energies and give energy levels allowing computations of thermodynamic quantities (see for example Ref. 172). For larger clusters, the potential energy surface can be used to compute the Hessian and proceed in the standard way to obtain thermodynamic quantities in the harmonic approximation.

Popelier commented:

Question 1: Let us take a single molecule, such as $Br(CH_2)_{10}Br$, and curl back its chain so that the two Br atoms end up in close contact but without being bonded. Surely there is a dispersion-like interaction between the two Br atoms but can SAPT, as presented in this article, calculate its energy value? SAPT's basic assumption is the partitioning of the total Hamiltonian into a sum of Hamiltonians of separated monomers. However, $Br(CH_2)_{10}Br$ is a single molecule and cannot be separated into monomers. Is there a conceptual challenge in partitioning the Hamiltonian for this covalently bound system, in the absence of monomers? Is a way forward the "atomic SAPT partition" or A-SAPT (J. Chem. Phys. **2014**, *141*, 044115)? However, A-SAPT struggles to produce chemically useful partitions of the electrostatic energy, caused by the buildup of oscillating partial charges on adjacent functional groups. This is why "functional-group SAPT" or F-SAPT (J. Chem. Theor. Comp. **2014**, *10*, 4417) was proposed. But then F-SAPT is formulated entirely in terms of fragments with integral charge (including zero), which may suit this molecule but which is not realistic in general.

Reply:

Yes, SAPT is a theory starting with the assumption that the system separates into a set of monomers at infinite distances from each other and these monomers are well-defined molecules (not necessarily closed-shell). As discussed above, this separation should not involve any breaking of chemical bonds. Thus, standard SAPT cannot be applied to $Br(CH_2)_{10}Br$.

A-SAPT and F-SAPT have been proposed with the goal to approximately assign interaction energy contributions to atoms or groups of atoms in the standard SAPT approach involving dimers of two closed-shell monomers. An extension of SAPT to intramonomer NCIs, named ISAPT, was proposed later[173]. Another approach of this type was developed in Ref. 174. One should emphasize that all intramolecular SAPT applications require one to make several assumptions and that different but equally reasonable assumptions can lead to very different predictions for a given system.

Popelier commented:

Question 2: It is stated that SAPT defines energy contributions each of which results from a differential equation that has an exact solution. Please give examples of such differential equations as they do not seem to appear in the standard SAPT literature.

Reply:

The differential equations for the wave function corrections are the foundations of RSPT. Such equations appear in many papers developing SAPT, see for example Eqs. (5), (10), and (27) in Ref. 21 and Eqs. (18), (29), (A.4), and (A.12) in the present work.

Popelier commented:

Question 3: Does the author agree with the opinion of Konrad Patkowski who writes in reference 58 that *"my personal least favorite SAPT term is the $\delta E_{HF}^{(2)}$ correction of Equation (20) (…). I consider its presence as an admission that pure SAPT has a difficulty that cannot be fully resolved from within, and it requires outside help in a form of supermolecular HF"*? Note that his Eq. (20) is the same as Eq. (7) in the current article and hence $\delta E_{HF}^{(2)} = \delta E_{\mathrm{int,resp}}^{\mathrm{HF}}$.

Reply:

As already discussed above, from the practical point of view the addition of $\delta E_{\mathrm{int,resp}}^{\mathrm{HF}}$ poses no problems. It does account for higher-order induction and exchange-induction effects and the errors introduced by this addition are very small. Furthermore, for nonpolar and mildly polar systems the addition of $\delta E_{\mathrm{int,resp}}^{\mathrm{HF}}$ is not needed if the third-order SAPT interaction energies are computed[108]. Thus, the issue is more of aesthetic than practical nature. It may be possible to increase the range of systems that do not need $\delta E_{\mathrm{int,resp}}^{\mathrm{HF}}$ by removing some approximations in the present set of third-order terms. Another possible step in this direction is to apply the formula for the second-order induction wave function derived in the present work in computations of the fourth- and fifth-order induction energy corrections. One more possible avenue is to make the regularized SAPT[18,88] applicable to general monomers (the regularized SAPT exhibits a faster convergence of induction energies).

Popelier commented:

Question 4: It is stated that *"One cannot uniquely determine the total charge transferred from monomer A to monomer B since this requires choosing an arbitrary boundary between the monomers."* The claim that charge cannot be uniquely assigned to atoms or even molecules is typically perpetuated, yet there is a great need to do so both in terms of interpretative (quantum) chemistry and force field construction. Which criterion (or criteria) give(s) rise to uniqueness if it is not experimental arbitration? According to this article, present-day SAPT ("*the* theory of intermolecular forces (…) providing the 'standard model' for EDA methods") is declared unique because the symmetrised Rayleigh-Schrödinger method is the only one used in practice. With such perhaps relaxed uniqueness criterion, can Occam's razor not be used to propose the topological partitioning as a satisfactory method to settle the debate on how to quantify charge transfer (even at the level of tens of millielectrons)? Moreover, an extensive and thorough comparison between fuzzy (interpenetrating) and nonfuzzy (space-filling, e.g., QTAIM) partitioning methods (J. Comp. Chem. **2007**, *28*, 161) showed that the latter *"may be preferred from the chemical consistency point of view" as they also "better preserve the atomic or fragment identity from the energetic point of view".*

Reply:

First, we changed the terminology to "reference model". Nevertheless, we maintain that SAPT components are the quantities that EDA methods should compare to (and mostly do). As discussed in the reply to Mo *et al.*, there is, actually, reasonably convincing experimental evidence for the physical character of SAPT components.

Also in the reply to Mo *et al.*, we have extensively discussed our position on charge delocalization. Of course, AIM-atoms give a possible definition of charge delocalization, but still do not allow to determine its energetic effect using SAPT.

Popelier commented:

Question 5: Can SAPT match the quantification of steric effects that the Interacting Quantum Atoms (IQA) method is able to achieve (J. Phys. Chem. A **2016**, *120*, 9647; ChemPhysChem **2021**, *22*, 775; Chemistry Open **2019**, *8*, 560)?

Reply:

As stated in the quote from Richard Feynman in the Introduction, molecules are "repelling upon being squeezed into one another". A simple interpretation relates this repulsion to steric effects: since atoms are approximately spherical, a molecule can be viewed as a shape resulting from superposition of such spheres, and if two interacting molecules come close enough to each other, the penetration of the spheres results in a repulsion. The more the spheres overlap, the larger the repulsive component becomes. In force fields, the repulsive effects are approximated by exponential terms or by large inverse powers of R (mostly $1/R^{12}$) with positive coefficients. SAPT, of course, accounts for steric effects, as demonstrated by the fact that SAPT PESs are accurate in the repulsive regions. The steric effects computed using SAPT cannot be compared with those computed using IQA as the two quantities are defined in different and unrelated ways. We would like to reiterate here that, as it is extensively discussed in Sec. III D, SAPT provides physical interpretation of the steric interactions grounded in quantum mechanics. The main repulsive effect comes from the first-order exchange energy, Eq. (43). Although, as discussed in Sec. III D, the exchange interactions are due to electron tunneling between monomers and not to overlap of wave functions, this tunneling is proportional to such overlap and can be modelled using overlap integrals[175–177].

The exchange interactions appear also in the second-order of SAPT, see Eqs. (46) and (47). These exchange energies are repulsive as well, but significantly smaller than the first-order ones. They are also proportional to overlap integrals. Another group of effects related to the wave-function overlap are damping effects[53,79–82]. In most cases, damping leads to positive contributions to interaction energies, however, as discussed briefly in the Introduction, it can also produce negative contributions, which then violate the simple steric interactions picture. Since the first-order exchange energy dominates the repulsive interactions, the values of this component presented in Table I provide a reasonable approximation of the total steric effect.

An example of unusual steric effects on shapes of PESs is provided in a recent study of the ammonia dimer[178]. This PES is very unusual in that it has a very narrow canyon-like valley where two equivalent minima are located, with a very small barrier between them at the lowest-energy saddle point. An overlap-driven variation of the components in the direction perpendicular to the interconversion path through this saddle, i.e., across the valley, explains the narrowness of this valley. One has to consider both the exchange and damping effects to get a complete explanation.

Appendix: Declarations

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Conflicts of interest:

None.

Availability of data and material:

Not applicable.

Code availability:

Not applicable.

Authors' contributions:

Both authors contributed equally.

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