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Size consistency and counterpoise correction in explicitly correlated calculations of interaction energies and interaction-induced properties

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Explicitly correlated calculations of interaction energies with wave functions that include all interparticle distances have suffered so far from the lack of size consistency resulting from the difficulty of defining monomer energies corresponding to the applied dimer basis. As a consequence, it has not been possible to obtain interaction energies vanishing at infinite intermonomer distance R. This has dramatically reduced the accuracy of calculations at distances where the error in the dimer energy was comparable with the interaction energy itself. The same problem occurs in calculations of interaction-induced properties. In this paper, we show how to circumvent this difficulty and obtain interaction energies or interaction-induced properties that vanish at large R. This is achieved by relaxing the Pauli principle in the diagonalization of the Hamiltonian of noninteracting monomers. The basis functions used for this diagonalization belong to the representation of the permutation group of the dimer induced by the product of representations appropriate for the monomer spin states. Nonlinear parameters of the basis set are optimized only for the dimer in the Pauli-allowed sector of the Hilbert space. In this way, one obtains R-dependent energy of noninteracting monomers and the corresponding interaction energy includes a counterpoise correction for the basis set superposition error. The efficiency of this procedure is demonstrated for the interaction of two hydrogen atoms where accurate reference data are known.

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I. INTRODUCTION

In many applications of electronic structure theory, one is concerned with changes of a certain property of the system resulting from interactions with other atoms and molecules. In the special case when the property of interest is expressed as an expectation value of a Hermitian operator $\hat{X}$, one considers the following quantity,

$$\Delta X = \langle\psi|\hat{X}\psi\rangle - \langle\psi_A|\hat{X}_A\psi_A\rangle - \langle\psi_B|\hat{X}_B\psi_B\rangle, \qquad (1)$$

for a system described by the wave function ψ and composed of two subsystems (monomers A, B) with the wave functions ψ_A, ψ_B. The operators $\hat{X}_A$ and $\hat{X}_B$ are defined analogously to $\hat{X}$, but involve summations over only the particles belonging to the subsystems A and B, respectively. Note that in the general case $\hat{X} \neq \hat{X}_A + \hat{X}_B$. The difference, ΔX, depends on the distance, R, between the interacting systems and possibly their mutual orientations. If the operator $\hat{X}$ is the Hamiltonian of the system, the quantity ΔX is called the interaction energy or the Born-Oppenheimer (BO) interaction potential. Otherwise, the name *interaction-induced* (or collision-induced) property is used.

Any interaction-induced property can, in principle, be calculated with help of Eq. (1)—this constitutes the so-called supermolecular approach. In fact, most calculations of ΔX rely on the supermolecular approach since the standard electronic structure methods are unable to yield the difference ΔX directly. A notable exception from this rule is the symmetry-adapted perturbation theory (SAPT); see Refs. [1–4] for an extended survey.

The biggest drawback of the supermolecular method is that it involves a significant degree of cancellation between the terms of Eq. (1). This is especially problematic in weakly interacting systems where the value of ΔX can be several orders of magnitude smaller than the subtracted terms on the right-hand-side of Eq. (1). In practice, ΔX is often smaller than the errors of computing the individual terms in Eq. (1).

A remedy for this problem is to calculate all terms on the right-hand-side of Eq. (1) in a consistent manner, so that these errors cancel out to a large extent, leaving an accurate value of ΔX. To achieve this, one has to use electronic structure methods that are size consistent, i.e., the energies or properties of the system tend to the correct limit (the sum of energies or properties of noninteracting monomers) when the distance between the subsystems grows to infinity [5]. The size-consistency requirement is critically important and is one of the factors which has led to the success and widespread popularity of the coupled-cluster theory; see Ref. [6] and references therein.

Even if the applied electronic structure model is size consistent, one has to face a problem stemming from the use of finite basis set expansion of wave functions used in Eq. (1). When the dimer and monomer energies are evaluated using their respective basis sets, the dimer energy is artificially lowered as the monomers in the dimer calculations have access to a larger basis set than their own basis. It has been recognized a long time ago [7–9] that this artificial lowering, referred to as the basis set superposition error (BSSE), cannot be viewed as a legitimate part of the interaction energy. In calculations employing one-electron basis sets (algebraic approximation),

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a prescription for removing the BSSE, called the counterpoise (CP) correction, was proposed by Boys and Bernardi [10]. It amounts to performing calculations for the monomers by using the whole dimer basis set [10,11]. While there is still an ongoing discussion in the literature about the applicability of this scheme [12–21], especially when the monomers undergo geometrical deformations [22–24], when small basis sets are used [25,26], or when basis set extrapolation schemes are employed [27,28], the CP correction is nowadays universally accepted as a default *a posteriori* method for elimination of BSSE.

Unfortunately, the situation is different in explicitly correlated methods which include all interparticle distances directly into trial wave functions. Since these wave functions are no longer composed solely of products of orbitals, it is not clear how to define a monomer basis set that would correspond to a given dimer basis and thus would allow consistent dimer and monomer calculations (and an error cancellation). In other words, in explicitly correlated calculations it has not been possible thus far to compute the monomer quantities in Eq. (1) in such a way that ΔX vanishes in the limit of infinite monomer separations.

In this paper, we show how to solve this difficulty. We consider the explicitly correlated Gaussian (ECG) basis, which is arguably the most efficient basis for solving both clamped-nuclei and fully nonadiabatic Schrödinger equation for few-body systems [29,30]. It has been successfully applied both to light atoms and to small molecules, and in many cases the results obtained with ECG are the most accurate to date [31–40]. It should be stressed, however, that the method proposed by us can also be applied to calculations with Slater geminals [41–44], Hylleraas configuration interaction expansions [45–47], and other multielectron basis sets where finite basis size consistency problem arises.

It should be noted that attempts to achieve the size consistency of the ECG method or to reduce the impact of its violation have been made and are described in the literature. Conceptually the simplest yet practically the most challenging strategy is to calculate the dimer term in Eq. (1) as accurately as possible and use the exact or near-exact monomer values to get ΔX. This brute-force approach typically works well for separations where ΔX is much larger than the error in $\langle\psi|\hat{X}\psi\rangle$. However, it does nothing to restore the size consistency. As ΔX does not vanish at large R, the results deteriorate strongly with increasing R and are difficult to match to an appropriate asymptotic formula. Examples of brute-force ECG calculations can be found, for example, in Refs. [48,49].

Another strategy, called the *monomer-contraction* (MC) method, has been proposed by Cencek *et al.* [33,34,50]. The main idea of this method is to build the product of the best available monomer wave functions into the dimer basis and represent ψ as

$$\psi = c_0\Pi(\psi_A\psi_B) + \sum_k c_k\phi_k, \qquad (2)$$

where ψ_A, ψ_B are wave functions optimized separately for monomers A and B, and fixed during the calculations for the dimer, Π is a projection operator ensuring that ψ has the correct permutation and spatial symmetry, and ϕ_k are elements of the conventional ECG basis for the dimer. The rationale behind the MC method is that if the monomer wave functions are accurate enough, the nonlinear optimization of ϕ_k is directed mostly toward the interaction-induced part of the dimer wave function. The monomer quantities entering Eq. (1) can be computed from ψ_A, ψ_B or more accurate literature values can be used if available. While this approach does not fully eliminate the error due to size inconsistency and, consequently, the accuracy breakdown at large R, it has been shown to give very accurate results for the helium dimer in the area of the van der Waals well [40].

A different approach to solve the size-consistency problem in the ECG method was proposed by Piszczatowski *et al.* [51]. In this approach, related to SAPT but not relying on the convergence of a perturbation expansion, the difference ΔX is computed directly and, by construction, vanishes at large R. However, this method is much more computationally expensive than the previous two, as there is a need to solve a set of response equations for each property of interest. This method has never been applied to the interaction energy itself.

In the subsequent sections, we shall present our method to achieve size consistency and to eliminate BSSE in explicitly correlated calculations and demonstrate its usefulness for the ECG wave functions. Specifically, we shall show how to calculate the R-dependent sum of monomer energies (or other properties), corresponding to a given basis set of the dimer, such that ΔX vanishes at large R. Therefore, the method can be viewed as a generalization of the conventional CP correction [10] beyond the orbital approximation. In fact, our CP correction plays a much more important role than in the orbital calculations because without it finite basis set explicitly correlated calculations are not size consistent. Taking the interaction of hydrogen atoms as a model system, for which practically exact results are known, we shall demonstrate numerically that the proposed technique guarantees size consistency both in calculations of the interaction energy and interaction-induced properties.

Atomic units are used throughout the present work unless explicitly stated otherwise.

II. THEORY

We assume that the wave functions ψ, ψ_A, and ψ_B, employed in Eq. (1) to compute ΔX, are approximations to the exact eigenfunctions of the electronic Hamiltonians $\hat{H}$, $\hat{H}_A$, and $\hat{H}_B$ and are obtained using the Rayleigh-Ritz variational procedure with the ECG basis. For a diatomic molecule (or a dimer) consisting of atoms with N_A and N_B electrons, the generic ECG function can be expressed in the form

$$\phi = \prod_{i=1}^{N} e^{-\alpha_i|\boldsymbol{r}_i-\boldsymbol{a}|^2} \prod_{i=1}^{N} e^{-\beta_i|\boldsymbol{r}_i-\boldsymbol{b}|^2} \prod_{i>j=1}^{N} e^{-\gamma_{ij}|\boldsymbol{r}_i-\boldsymbol{r}_j|^2}, \qquad (3)$$

where $\boldsymbol{r}_i$, $i = 1, \ldots, N$, are vectors containing Cartesian coordinates of electrons, $\boldsymbol{a}$ and $\boldsymbol{b}$ are vectors specifying the nuclear positions, $R = |\boldsymbol{a}-\boldsymbol{b}|$, and $N = N_A + N_B$. The exponents α_i, β_j, and γ_{ij} are different for each basis function and are optimized by minimizing the lowest eigenvalue of the Hamiltonian matrix. For simplicity, we assumed that the dimer is in a Σ^+ state. The functions of the form of Eq. (3)

constitute a potentially complete basis set in the space of Σ^+ symmetry [52,53]. To construct ECGs of other symmetries, one can follow the prescription of Ref. [52]. The ECG basis functions for the monomer A (B) can also be expressed using Eq. (3), provided that N is replaced by N_A (N_B) and the factors $e^{-\beta_i|\boldsymbol{r}_i-\boldsymbol{b}|^2}$ ($e^{-\alpha_i|\boldsymbol{r}_i-\boldsymbol{a}|^2}$) are eliminated.

We assume that the Hamiltonians $\hat{H}$, $\hat{H}_A$, and $\hat{H}_B$ are nonrelativistic and do not act on spin variables. Therefore, we can employ the spin-free formalism where the correct spin symmetry and fulfillment of the Pauli exclusion principle are simultaneously guaranteed by imposing the appropriate permutation symmetry of the wave function [54–56]. Specifically, for a system with N electrons and spin S, the wave function must transform according to the irreducible representation of the permutation group S_N corresponding to the Young diagram containing $N/2-S$ rows of length 2 and $2S$ rows of length 1, denoted conventionally as $[2^{N/2-S}1^{2S}]$. This symmetry of the wave function can be enforced with the help of appropriate Young operators [56]. Within the present computational capabilities, this spin-free ECG method is applicable to systems containing up to seven or eight active particles; see Refs. [57,58] as a representative examples.

By inspection of Eq. (3), we see that for a given N-electron dimer basis it is difficult to construct the corresponding N_A-electron and N_B-electron bases for the monomers such that finite basis set calculations will be size consistent. Indeed, to the best of our knowledge, no such construction has been proposed in the literature. One reason for this difficulty is the inherent delocalization of the dimer basis set functions. Another reason is the fact that the basis functions used to expand ψ and ψ_A or ψ_B depend on different number of electrons. The latter difficulty can be circumvented if Eq. (1) is rewritten in the form

$$\Delta X = \langle\psi|\hat{X}\psi\rangle - \langle\psi_0|\hat{X}_0\psi_0\rangle, \tag{4}$$

where $\hat{X}_0 = \hat{X}_A + \hat{X}_B$, and $\psi_0 = \psi_A\psi_B$ is the appropriate eigenfunction of $\hat{H}_0 = \hat{H}_A + \hat{H}_B$, i.e.,

$$\hat{H}_0\psi_0 = (E_A + E_B)\psi_0, \tag{5}$$

where $E_A = \langle\psi_A|\hat{H}_A\psi_A\rangle$ and $E_B = \langle\psi_B|\hat{H}_B\psi_B\rangle$. We assume for simplicity that the E_0 level of $\hat{H}_0$ is nondegenerate. The functions ψ and ψ_0 depend on the same number electronic coordinates and thus can, in principle, be obtained by diagonalizing matrices of the Hamiltonians $\hat{H}$ and $\hat{H}_0$, respectively, within the same basis set. The calculations performed in this way would indeed be consistent, so that one could expect both the error cancellations to occur and ΔX to correctly vanish at large separations.

The problem with this idea is that ψ and ψ_0 have different symmetries and, even at large R, reside in distant locations of the Hilbert space [59]. This is a consequence of the fact that $\hat{H}$ and $\hat{H}_0$ have different symmetry groups, denoted by $\mathcal{G}$ and $\mathcal{G}_0$ further in the text. It is impossible to perform calculations for ψ and ψ_0 in a common basis adapted to irreducible representations of both $\mathcal{G}$ and $\mathcal{G}_0$. The main idea of our method is to perform calculations with the basis that is adapted to $\mathcal{G}\cap\mathcal{G}_0$, i.e., the largest subgroup of $\mathcal{G}$ and $\mathcal{G}_0$. To guarantee that ψ is a pure spin state, we also impose the condition that this basis is invariant under all operations of $\mathcal{G}$.

To illustrate this idea with a simple example, we assume that A and B are ground-state hydrogen atoms. In this case, $\mathcal{G} = D_{\infty h}\times S_2$ and $\mathcal{G}_0 = O_{\boldsymbol{a}}(3)\times O_{\boldsymbol{b}}(3)\times G_I$, where $O_{\boldsymbol{a}}(3)$ and $O_{\boldsymbol{b}}(3)$ are symmetry groups of H_A and H_B, respectively, and $G_I = \{E, P^*\}$ is the two-element group containing the identity element E and the permutation-inversion operation $P^* = \hat{I}P_{12}$. The latter is a combination of the inversion $\hat{I}$ with respect to the center of the diatom and the transposition P_{ij} of the coordinates of the ith and jth electrons. The groups $O_{\boldsymbol{a}}(3)$ and $O_{\boldsymbol{b}}(3)$ contain all rotations and the inversion with respect to the respective nuclear positions $\boldsymbol{a}$ and $\boldsymbol{b}$ (the accidental SO(4) symmetry of hydrogen atom can be neglected as it is not relevant in further discussion).

It is easy to see that the largest common subgroup of $\mathcal{G}$ and $\mathcal{G}_0$ is the group $C_{\infty v}\times G_I$. The primitive ECG function of Eq. (3) is already adapted to $C_{\infty v}$. To additionally adapt this basis to G_I, we project it with $(1+P^*)/2$ (we take the plus sign in the projector since both ψ_0 and ψ are symmetric under the action of P^*). The basis adapted to $\mathcal{G}\cap\mathcal{G}_0$ consists thus of functions of the form

$$\begin{aligned}\phi' = {} & e^{-\alpha_1 r_{a1}^2}\, e^{-\alpha_2 r_{b1}^2}\, e^{-\beta_1 r_{a2}^2}\, e^{-\beta_2 r_{b2}^2}\, e^{-\gamma_{ij} r_{12}^2} \\ & + e^{-\beta_2 r_{a1}^2}\, e^{-\beta_1 r_{b1}^2}\, e^{-\alpha_2 r_{a2}^2}\, e^{-\alpha_1 r_{b2}^2}\, e^{-\gamma_{ij} r_{12}^2},\end{aligned} \tag{6}$$

where $r_{ai} = |\boldsymbol{r}_i - \boldsymbol{a}|$, $r_{bi} = |\boldsymbol{r}_i - \boldsymbol{b}|$, and $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$. This basis is not invariant under the operations of $\mathcal{G}$, so we have to augment it by adding functions $\hat{I}\phi'$ and $P_{12}\phi'$. Both augmentations lead to the same result, so the final basis consists of functions of the form of ϕ' and $P_{12}\phi'$. In Sec. III, we shall show that variational Rayleigh-Ritz calculations employing this basis both for the dimer and for the monomer (diagonalizing the $\hat{H}$ and $\hat{H}_0$ Hamiltonians, respectively, and optimizing nonlinear parameters only at the dimer level) are consistent in the sense that the monomer errors cancel out and the interaction energy approaches zero at infinity. In practice, is it useful to follow the idea of the monomer-contraction method [33,34,50] and extend this basis by two additional functions: $\tilde{\psi}_A\tilde{\psi}_B$ and $P_{12}\tilde{\psi}_A\tilde{\psi}_B$, where $\tilde{\psi}_A$ is the best available ECG approximation of the wave function for atom A and $\tilde{\psi}_B = P^*\tilde{\psi}_A$. These two basis functions are fixed and, unlike all functions of the form ϕ' and $P_{12}\phi'$, are not subject to the nonlinear optimization.

Since the nonlinear optimization performed at the dimer level is very time-consuming, it is useful to adapt the whole basis at this stage of calculations. This is possible since the whole basis is invariant under the operations of the dimer symmetry group $\mathcal{G}$. If one is interested in the triplet ${}^3\Sigma_u^+$ state, then the size of the basis can be reduced by the factor of 2 by taking only the functions of the form $(1-P_{12})\phi'$ [plus possibly the single function $(1-P_{12})\tilde{\psi}_A\tilde{\psi}_B$]. These basis functions are obviously antisymmetric under P_{12} (are triplet functions) but are also ungerade under the action of the inversion operator $\hat{I}$ since $\hat{I}\phi' = P_{12}\phi'$ and, consequently,

$$\hat{I}(1-P_{12})\phi' = -(1-\hat{I})\phi' = -(1-P_{12})\phi'. \tag{7}$$

It is easy to verify that Eq. (7) holds also when ϕ' is replaced by $\tilde{\psi}_A\tilde{\psi}_B$ and that the singlet functions obtained by the symmetrization $1+P_{12}$ have gerade symmetry, i.e., are invariant under the inversion $\hat{I}$. It should be emphasized that a simple diagonalization of H_0 in the space of antisymmetric functions

$(1 - P_{12})\phi'$ only would lead to a completely wrong energy E_0 since at large R the exact function ψ_0 has equally large components in the spaces of symmetric and antisymmetric functions. Thus, the diagonalization of H_0 and calculation of E_0 must be done in the space containing functions of both symmetries, i.e., in the space containing both ϕ' and $P_{12}\phi'$.

When the interacting one-electron systems are different, as in the case of $\mathrm{He}^+ \ldots \mathrm{H}$ interaction, $\mathcal{G} = C_{\infty v} \times \mathrm{S}_2$, $\mathcal{G}_0 = O_{\boldsymbol{a}}(3) \times O_{\boldsymbol{b}}(3)$, and $\mathcal{G} \cap \mathcal{G}_0 = C_{\infty v}$. The inversion symmetry is not present and the basis for the monomer calculations is constructed from the functions ϕ and $P_{12}\phi$, where ϕ is the two-electron primitive ECG [given by the first term on the right-hand side of Eq. (6)]. In the dimer calculations (involving the optimization of the nonlinear parameters), the basis is half as large and consists of the functions $(1 - P_{12})\phi$ (for the triplet state).

The generalization of this construction to the interaction of many-electron atoms is natural but technically somewhat complicated as a result of the multidimensionality of the representations of the permutation group. The dimer group $\mathcal{G}$ contains now the factor S_N instead of S_2 and one has to include in $\mathcal{G}_0$ the product $\mathrm{S}_{N_A} \times \mathrm{S}_{N_B}$ of the monomer permutation groups. As for the H_2, the basis is constructed in two steps. First, the primitive ECG basis of Eq. (3) is adapted to the appropriate irreducible representation Γ_0 of $\mathcal{G} \cap \mathcal{G}_0$. Next, one forms the basis of the induced representation $\Gamma \uparrow \mathcal{G}$ and takes the functions adapted simultaneously to Γ_0 and to the irreducible representations of $\mathcal{G}$ entering $\Gamma_0 \uparrow \mathcal{G}$. Below we shall illustrate this general procedure with three simple but typical examples.

Example 1: Interaction of a singlet helium atom with a hydrogen atom

In this case, the dimer symmetry is $\mathcal{G} = C_{\infty v} \times \mathrm{S}_3$, while $\mathcal{G}_0 = O_{\boldsymbol{a}}(3) \times O_{\boldsymbol{b}}(3) \times \mathrm{S}_2$, and $\mathcal{G} \cap \mathcal{G}_0 = C_{\infty v} \times \mathrm{S}_2$. For the singlet state of helium, the function $\psi_0 = \psi_{\mathrm{He}}\psi_{\mathrm{H}}$ is symmetric under the permutation P_{12} and the molecular ${}^2\Sigma^+$ function can be chosen to be symmetric under P_{12} as well. Therefore, we can symmetrize the ECG basis and consider further the functions $\phi' = (1 + P_{12})\phi$, where ϕ is a primitive, three-electron, two-center ECG function of the form of Eq. (3). To obtain the basis invariance under the action of S_3, we have to perform the induction process, i.e., act on ϕ' with all permutations from S_3. In this way, we obtain three ECG functions ϕ', $P_{13}\phi'$, and $P_{23}\phi'$, forming a basis for the induced representation $[2] \uparrow \mathrm{S}_3$. The representation $[2] \uparrow \mathrm{S}_3$, referred to also as the outer product $[2] \otimes [1]$ (see Ref. [56]), is reducible and decomposes as

$$[2] \uparrow \mathrm{S}_3 = [21] + [3]. \tag{8}$$

which can also be represented with help of the Young diagrams as

$$\begin{array}{|c|c|}\hline & \\ \hline \end{array} \otimes \begin{array}{|c|}\hline \\ \hline \end{array} = \begin{array}{|c|c|}\hline & \\ \hline \\ \cline{1-1} \end{array} + \begin{array}{|c|c|c|}\hline & & \\ \hline \end{array} \; . \tag{9}$$

One of the two functions transforming according to the [21] representation is antisymmetric under the action of P_{12} and can be disregarded. We are left with the functions

$$\phi'' = (2 - P_{13} - P_{23})\phi' \tag{10}$$

that can be used in calculations of the physical, spin doublet state of the molecule, and the functions

$$\phi''' = (1 + P_{13} + P_{23})\phi' \tag{11}$$

that are Pauli forbidden (cannot be used to construct an antisymmetric spin-dependent function) but must be used together with ϕ'' in consistent calculation of the sum of monomer energies. Equation (10) can be obtained by acting on ϕ' with the character projector of the [21] representation of S_3, or directly from ϕ by acting with the Young operator $\omega_{11}^{[21]}$ corresponding to the orthogonal Young-Yamanouchi representation [21] of S_3. In general,

$$\omega_{rt}^{[\lambda]} = \sum_{P \in S_N} \Gamma_{rt}^{[\lambda]}(P)\, P, \tag{12}$$

where $\Gamma_{rt}^{[\lambda]}(P)$ are matrices of the representation $[\lambda]$ [56]. Since the nonlinear parameters are optimized only for the dimer, these parameters are identical in ϕ''' and ϕ''. Equations (8) and (11) show that to obtain size-consistent energy one has to violate the Pauli principle in calculations of the sum of the monomer energies.

Example 2: Interaction of a doublet lithium atom with a hydrogen atom

This case considered, e.g., in Refs. [54,55], is somewhat more complicated, since we have the exchange degeneracy for lithium and the S_4 group is larger than S_3. The groups $\mathcal{G}$, $\mathcal{G}_0$, and $\mathcal{G} \cap \mathcal{G}_0$ are the same as in the previous example except that the S_3 factor in $\mathcal{G}$ is replaced by S_4, and the S_2 factor in $\mathcal{G}_0$ by S_3. The doublet states of lithium exhibit (unphysical) exchange degeneracy since the [21] representation is two dimensional and we have two standard Young tableaux

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1} \end{array} \quad \text{and} \quad \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1} \end{array} \; . \tag{13}$$

We (arbitrarily) chose the first one and require that the lithium wave function ψ_{Li} as well as the molecular function ψ_{LiH} be symmetric with respect of the exchange of the electrons 1 and 2. Thus, diagonalizations for both the supermolecule and the noninteracting monomers can be performed in the space with the permutational symmetry specified by the first tableau in Eq. (13). To construct a basis of this symmetry for consistent molecule and separated atom calculations, we start by projecting the primitive four-electron ECG function of Eq. (3) with $\omega_{11}^{[21]}$,

$$\phi' = (2 - P_{13} - P_{23})(1 + P_{12})\phi, \tag{14}$$

and generate the induced representation by acting on ϕ' with all S_4 permutations. Using, e.g., the Littlewood theorem for the outer product decomposition [56], we find

$$[21] \uparrow \mathrm{S}_4 = [31] \;+\; [22] \;+\; [211]. \tag{15}$$

or by using the Young diagrams

$$\begin{array}{|c|c|}\hline & \\ \hline \\ \cline{1-1} \end{array} \otimes \begin{array}{|c|}\hline \\ \hline \end{array} = \begin{array}{|c|c|c|}\hline & & \\ \hline \\ \cline{1-1} \end{array} + \begin{array}{|c|c|}\hline & \\ \hline & \\ \hline \end{array} + \begin{array}{|c|c|}\hline & \\ \hline \\ \cline{1-1} \\ \cline{1-1} \end{array} \; . \tag{16}$$

The dimension of the $[21] \uparrow \mathrm{S}_4$ representation is 8 but by inspecting the standard Young tableaux we find that there are only three functions of the S_3 symmetry corresponding to the first tableau of Eq. (13). These three functions can be obtained directly from ϕ using the Young operators $\omega_{22}^{[31]}$, $\omega_{11}^{[22]}$, and $\omega_{11}^{[211]}$ or by acting with the [31], [22], and [211] character projectors on ϕ'. The explicit form of these three functions is

$$\phi^{[31]} = (3 + P_{34})(1 + P_{14} + P_{24})\phi', \tag{17}$$

$$\phi^{[22]} = (1 + P_{34})(1 - P_{14} - P_{24})\phi', \tag{18}$$

$$\phi^{[211]} = (1 - P_{34})(3 - P_{14} - P_{24})\phi'. \tag{19}$$

If we are interested in the singlet or the triplet states, we use the functions of the form of $\phi^{[22]}$ or $\phi^{[211]}$, respectively, while for the monomer energy calculation we must use (without further nonlinear optimization) both of these functions plus the Pauli forbidden one, $\phi^{[31]}$. Thus, the basis of the monomer calculations is three times as large as in the dimer case.

Example 3: The ground state of the helium dimer

In this case, we have to consider both the permutation and the inversion symmetry. The groups $\mathcal{G}$, $\mathcal{G}_0$ and $\mathcal{G} \cap \mathcal{G}_0$ have now the following direct product structure: $\mathcal{G} = D_{\infty h} \times \mathrm{S}_4$, $\mathcal{G}_0 = O_{\boldsymbol{a}}(3) \times O_{\boldsymbol{b}}(3) \times \mathrm{S}_2 \times \mathrm{S}_2 \times \mathcal{G}_I$, and $\mathcal{G} \cap \mathcal{G}_0 = \mathrm{C}_{\infty v} \times \mathrm{S}_2 \times \mathrm{S}_2 \times \mathcal{G}_I$, where $\mathcal{G}_I = \{E, \hat{I}P_{ab}\}$ is a two-element group containing the product of the inversion operation $\hat{I}$ and a permutation P_{ab} that swaps all electrons between atoms A and B. Assuming that H_A and H_B act on electrons 1,2 and 3,4, respectively, the permutation P_{ab} can be taken arbitrarily as any of the four $P_{13}P_{24}$, $P_{14}P_{23}$, P_{1324}, or P_{1423} without changing the $\mathrm{S}_2 \times \mathrm{S}_2 \times \mathcal{G}_I$ group.

Since we are interested in the interaction of singlet states, we can adapt the ECG basis to the fully symmetric representation of $\mathcal{G} \cap \mathcal{G}_0$ and use the symmetrized ECG functions of the form

$$\phi' = (1 + P_{12})(1 + P_{34})(1 + \hat{I}P_{ab})\phi, \tag{20}$$

where ϕ is the primitive ECG function of Eq. (3) with $N = 4$. Performing the induction of the fully symmetric representation of $\mathrm{S}_2 \times \mathrm{S}_2$ to S_4, one finds

$$[2] \times [2] \uparrow \mathrm{S}_4 = [4] + [31] + [22], \tag{21}$$

which can be written by using the Young diagrams as

$$\ydiagram{2} \otimes \ydiagram{2} = \ydiagram{4} + \ydiagram{3,1} + \ydiagram{2,2}\,. \tag{22}$$

The induction from $\mathrm{C}_{\infty v}$ to $D_{\infty h}$ is not needed since one can show that the space spanned by $P\phi'$, $P \in \mathrm{S}_4$ is invariant under the inversion $\hat{I}$. The induced representation $[2] \times [2] \uparrow \mathrm{S}_4$ is six dimensional but, since we can work only with functions fully symmetric under $\mathrm{S}_2 \times \mathrm{S}_2$, only three functions are necessary:

$$\phi^{[4]} = (1 + P_{13}P_{24} + P_{13} + P_{14} + P_{23} + P_{24})\phi', \tag{23}$$

$$\phi^{[31]} = (1 - P_{13}P_{24})\phi', \tag{24}$$

$$\phi^{[22]} = (2 + 2P_{13}P_{24} - P_{13} - P_{14} - P_{23} - P_{24})\phi'. \tag{25}$$

Only the last of these functions is Pauli allowed and appears in the dimer calculations. The first two are Pauli forbidden but must be used in calculations for the noninteracting monomers to obtain size-consistent results.

The functions $\phi^{[22]}$ and $\phi^{[4]}$ are already of the gerade symmetry under inversion. To prove this, we note that

$$\hat{I}\phi' = P_{ab}\,\phi' \tag{26}$$

for any of the four permutations P_{ab}. One can show that the parts of $\phi^{[4]}$ or $\phi^{[31]}$ generated by $1 + P_{13}P_{24}$, by $P_{13} + P_{24}$, and by $P_{23} + P_{14}$ are separately invariant under the action of $\hat{I}$. Specifically,

$$\hat{I}(P_{13}+P_{24})\phi' = (P_{13}+P_{24})P_{13}P_{24}\phi' = (P_{13}+P_{24})\phi',$$

$$\hat{I}(P_{23}+P_{14})\phi' = (P_{23}+P_{14})P_{23}P_{14}\phi' = (P_{23}+P_{14})\phi',$$

and similarly for $(1 + P_{13}P_{24})\phi'$. Analogously, one can show that $\phi^{[31]}$ is ungerade under inversion.

In all examples considered here, the induced representation is simply reducible. However, there are cases when there are multiplicities. For instance, for the interaction of three ground-state hydrogen atoms, the representation [21] occurs two times. Therefore, in the trimer calculations, we have two ECG functions of the [21] symmetry for one primitive ECG function. To obtain the energy of the monomers, all six ECG functions spanning the induced (regular in this case) representation must be used. Similar multiplicity problem occurs for the interaction of two doublet lithium atoms when the representation [321] appears two times in the direct product $[21] \otimes [21]$.

III. NUMERICAL RESULTS

A. Computational details

As a numerical illustration, we performed variational ECG calculations of the interaction energy of hydrogen atoms in the ground $({}^1\Sigma_g{}^+)$ state of H_2. We employed the monomer contraction method of Cencek *et al.* and assumed the trial wave function in the form

$$(1 + P_{12})\big(1 + \hat{I}\big)\left[c_0\,\phi_{1s}(r_{1a})\,\phi_{1s}(r_{2b}) + \sum_{k=1}^{K} c_k\phi_k\right], \tag{27}$$

where ϕ_k are the primitive geminal functions, cf. Eq. (3) with $N = 2$,

$$\phi_k = e^{-a_k r_{1a}^2 - b_k r_{1b}^2 - c_k r_{2a}^2 - d_k r_{2b}^2 - w_k r_{12}^2}, \tag{28}$$

and $\phi_{1s}(r)$ is the hydrogenic 1s orbital expanded as a linear combination of Gaussian 1s functions. Two distinct basis sets were optimized—the first composed of 150 geminal functions with the monomer contraction length of nine functions (9/150 basis set) and the second composed of 300 geminal functions with the monomer contraction length of twelve functions (12/300 basis set). The relevant properties of the hydrogen atom obtained for each monomer contraction function are given in Table I.

The nonlinear parameters a_k, b_k, etc., in all functions (28) were optimized to minimize the total energy of the molecule. We employed the conventional optimization strategy where the primitive functions are optimized one at a time using the Powell's conjugate direction method [60]. Technical details of this procedure can be found, for example, in Refs. [61,62]. About one thousand optimization sweeps over the whole basis set were performed for each internuclear distance. The

TABLE I. Properties of the hydrogen atom calculated with the orbital 1s expanded in 9 or 12 primitive Gaussian functions. E is the electronic energy and $\langle\delta(\mathbf{r})\rangle$ is the expectation value of δ distribution centered at the nucleus. Errors with respect to the exact values are given below each entry.

	9	12
E	−0.499 998 136	−0.499 999 904
Error	0.000 001 864	0.000 000 096
$\langle\delta(\mathbf{r})\rangle$	0.317 799 920	0.317 840 649
Error	0.000 509 966	0.000 469 238

monomer contraction functions were kept fixed during the optimization procedure. The distance-dependent energies of noninteracting monomers were obtained according to the prescription given in the previous section.

In the present case, the monomers are one-electron atoms and thus it would theoretically be possible to use even more accurate monomer contraction functions, i.e., accurate down to the level of the arithmetic precision. However, our goal here is to simulate the situation found in other systems, e.g., the helium dimer, where such accurate monomer contractions are practically unfeasible.

B. Interaction energies

The simplest numerical confirmation of the size consistency of the proposed counterpoise correction can be obtained by applying it to compute the interaction energy with only a single ECG basis set function. This test can be viewed as the most demanding one as it is well known that the size-consistency problems are much more pronounced in smaller basis sets. For the purposes of this test, we did not use the MC method. The single ECG basis function was optimized separately for each R to get the best possible energy of the molecule.

The results of the test for the hydrogen molecule are reported in Table II and demonstrate that the dimer energy and the energy of noninteracting monomers tend to the same value for large R. Thus, the interaction energy vanishes at large R and one obtains size-consistent results. It is of note that for $R > 7.0$ the energy of the noninteracting monomers becomes practically independent of R. We performed a similar test also for the HeH molecule in the ground ($^2\Sigma^+$) state; see Table III. This provides a verification that the proposed counterpoise correction works for a three-electron system with a nontrivial permutation symmetry. During the optimizations for the HeH molecule, we frequently encountered multiple local minima and had to pay attention to avoid jumping between them when the internuclear distance was increased. We checked that after applying the counterpoise correction the interaction energy vanished at large R, independently of which local minimum was selected in the calculations.

TABLE II. Dimer energy and the counterpoise-corrected energy of noninteracting atoms for the hydrogen molecule (H_2) in the $^1\Sigma_g^+$ state calculated with a single ECG function. The difference between the two energies is given in the last column. The symbol $X[\pm n]$ stands for $X \times 10^{\pm n}$.

R	Dimer energy	Monomer energies	Diff.
1.40	−1.080 150 157	−0.851 504 752	2.29[−1]
2.00	−1.047 848 806	−0.877 907 811	1.70[−1]
3.00	−0.962 272 248	−0.892 953 363	6.93[−2]
4.00	−0.916 883 089	−0.902 594 831	1.43[−2]
5.00	−0.906 403 817	−0.904 962 697	1.44[−3]
6.00	−0.905 161 164	−0.905 046 809	1.14[−4]
7.00	−0.905 054 674	−0.905 048 043	6.63[−6]
8.00	−0.905 048 301	−0.905 048 052	2.50[−7]
9.00	−0.905 048 057	−0.905 048 052	5.79[−9]
10.0	−0.905 048 052	−0.905 048 052	8.17[−11]

TABLE III. Molecule energy and the counterpoise-corrected energy of noninteracting atoms for the HeH molecule in the lowest $^2\Sigma^+$ state calculated with a single ECG function. The difference between the two energies is given in the last column. The symbol $X[\pm n]$ stands for $X \times 10^{\pm n}$.

R	Molecule energy	Monomer energies	Diff.
3.00	−2.761 101 011	−2.757 017 204	4.08[−3]
3.50	−2.755 780 617	−2.754 959 925	8.20[−4]
4.00	−2.753 543 972	−2.753 404 364	1.40[−4]
5.00	−2.751 558 211	−2.751 555 878	2.33[−6]
6.00	−2.750 556 963	−2.750 556 942	2.13[−8]
7.00	−2.749 956 748	−2.749 956 747	1.03[−9]
8.00	−2.749 568 092	−2.749 568 092	3.47[−10]

Let us now discuss calculations with a larger number of ECG functions. In Table IV, we present absolute errors in the interaction energy of H_2 obtained using the 9/150 and 12/300 basis sets. The reference values used in both tables are taken from the work of Pachucki [63] and can be considered exact for the present purposes. For each internuclear distance, the interaction energy was calculated employing the same total dimer energy and by subtracting:

(a) monomer energies calculated from the MC function alone (pure MC method);

(b) exact monomer energies (exact monomer method);

(c) the counterpoise-corrected energy of the noninteracting monomers calculated according to the scheme given in Sec. II (CP method);

(d) the large-R asymptotic energy of the noninteracting monomers; in practice, the energy of noninteracting monomers computed at the largest available interatomic distance (asymptotic CP method).

Table IV presents results near the minimum of the potential energy curve ($R = 1.4$) and in the long-range tail of the potential. It is clearly seen that the methods based on subtracting the exact or MC monomer energies are not size consistent, as the interaction energies calculated with these methods tend to some spurious nonzero values. This is best visible for the 9/150 basis set even for quite moderate R, whereas for the larger 12/300 basis set the deterioration of the results is less pronounced. In contrast, the counterpoise-corrected interaction energy vanishes as $R \to \infty$.

It is obvious that the relative errors in the interaction energies computed using the MC method or the exact monomer

TABLE IV. Absolute errors in the interaction energy of the hydrogen molecule ($^1\Sigma_g{}^+$ state) as a function of the internuclear distance (R). The symbol $X[\pm n]$ stands for $X \times 10^{\pm n}$.

	9/150				12/300				
R	MC	Exact mon.	CP	Asym. CP	MC	Exact mon.	CP	Asym. CP	Ref. [63]
1.0	−3.62[−6]	1.10[−7]	−2.05[−6]	8.65[−8]	−1.67[−7]	2.58[−8]	−5.13[−8]	2.16[−8]	−1.24540[−1]
1.4	−3.61[−6]	1.14[−7]	−2.07[−6]	9.02[−8]	−1.70[−7]	2.25[−8]	−7.57[−8]	1.83[−8]	−1.74476[−1]
2.0	−3.62[−6]	1.12[−7]	−2.35[−6]	8.82[−8]	−1.72[−7]	2.04[−8]	−9.53[−8]	1.62[−8]	−1.38133[−1]
4.0	−3.59[−6]	1.34[−7]	−1.15[−6]	1.11[−7]	−1.51[−7]	4.17[−8]	−1.54[−8]	3.75[−8]	−1.63903[−2]
6.0	−3.69[−6]	3.42[−8]	−4.87[−7]	1.09[−8]	−1.77[−7]	1.57[−8]	−1.75[−8]	1.15[−8]	−8.35708[−4]
7.0	−3.70[−6]	2.67[−8]	−2.07[−7]	3.43[−9]	−1.84[−7]	7.95[−9]	−1.11[−8]	3.77[−9]	−1.97914[−4]
8.0	−3.71[−6]	1.61[−8]	−6.15[−8]	−7.19[−9]	−1.88[−7]	4.65[−9]	−8.84[−9]	4.74[−10]	−5.56050[−5]
9.0	−3.71[−6]	1.61[−8]	−9.11[−8]	−7.18[−9]	−1.89[−7]	3.40[−9]	−2.40[−9]	−7.79[−10]	−1.97818[−5]
10.0	−3.71[−6]	1.47[−8]	−5.80[−8]	−8.66[−9]	−1.89[−7]	3.19[−9]	−4.25[−9]	−9.91[−10]	−8.75575[−6]
11.0	−3.72[−6]	1.11[−8]	−4.75[−8]	−1.22[−8]	−1.90[−7]	2.42[−9]	−3.52[−9]	−1.76[−9]	−4.50599[−6]
12.0	−3.72[−6]	1.31[−8]	−3.32[−8]	−1.02[−8]	−1.90[−7]	2.32[−9]	−1.65[−9]	−1.86[−9]	−2.54597[−6]
14.0	−3.71[−6]	1.32[−8]	−2.43[−8]	−1.01[−8]	−1.90[−7]	2.67[−9]	−1.50[−9]	−1.51[−9]	−9.60681[−7]
16.0	−3.71[−6]	1.45[−8]	−1.36[−8]	−8.84[−9]	−1.90[−7]	2.62[−9]	−1.34[−9]	−1.56[−9]	−4.19586[−7]
18.0	−3.71[−6]	1.45[−8]	−8.81[−9]	−8.81[−9]	−1.89[−7]	3.38[−9]	−8.01[−10]	−8.01[−10]	−2.03341[−7]

energies must grow to infinity at large R. Inspecting the results of Table IV, one can find, however, that the relative error in both CP approaches also grows with R although moderately. This seems discouraging but we believe that this is unavoidable in methods where the wave function is optimized variationally at each R. For large R, the monomer energies constitute the dominating contribution to the total energy of the supermolecule and thus the optimization is biased toward improving the monomer energies rather than describing the bonding. This is not a serious problem in practice since at very large R the interaction energy can be accurately represented by its asymptotic expansion based on monomer properties only (e.g., dynamic polarizabilities).

The main purpose of the present work was to correct the interaction energies in the long-range region, i.e., where the size-consistency errors are the most pronounced, but it is equally important to validate the proposed strategy for smaller internuclear separations. Rather surprisingly, the asymptotic CP turns out to be superior to other methods near the bottom of the potential energy curve and is capable of recovering at least one additional significant digit as compared with the CP technique. The method based on subtracting the exact monomer energies also gives at small R more accurate results than the CP method. This situation changes for larger R. When the 12/300 basis set is used, the relative error in the interaction energies calculated with the CP method becomes smaller already at $R \approx 12.0$. For large internuclear distances, the standard and asymptotic CP methods give, on average, results of a comparable quality. In view of its very good behavior at small R, the asymptotic CP appears to be the most promising method for calculation of accurate potential energy surfaces for larger systems. While this method introduces a degree of arbitrariness, i.e., the choice of a internuclear distance used to evaluate the noninteracting monomer energies, it seems to be a pragmatic way to extract the best possible results out of a given dimer wave function.

The sum of noninteracting monomer energies obtained with the counterpoise method is distance dependent, as in the standard Boys-Bernardi scheme. Therefore, it is interesting to investigate what is the dependence of this quantity on R. In Table V, we show results obtained with 9/150 and 12/300 basis sets. Near the bottom of the potential energy curve, the energy of noninteracting monomers is only slightly more accurate than the energy corresponding to the monomer contraction function. For example, with the 12/300 basis set at $R = 1.40$, the errors of these energies are 98 nH and 192 nH, respectively. In the region $R = 4.0$–10.0 the former error drops sharply by one to two orders of magnitude. This is a manifestation of the fact that for larger internuclear distances the optimization is biased toward the monomer. Finally, for $R > 12.0$ this error decays slowly or fluctuates around some constant value, amounting to about 30.0 nH and 4.0 nH for the 9/150 and 12/300 basis sets, respectively. These fluctuations are at a low 0.1 nH level and are artifacts of the nonlinear optimization procedure.

TABLE V. Absolute errors in the energy of two noninteracting hydrogen atoms (with respect to the exact value of −1) calculated with the counterpoise method as a function of the internuclear distance. $X[\pm n]$ stands for $X \times 10^{\pm n}$.

R	9/150	12/300
1.00	2.163[−6]	7.712[−8]
1.40	2.181[−6]	9.815[−8]
2.00	2.465[−6]	1.158[−7]
4.00	1.279[−6]	5.708[−8]
6.00	5.209[−7]	3.324[−8]
7.00	2.332[−7]	1.902[−8]
8.00	7.761[−8]	1.350[−8]
9.00	1.072[−7]	5.799[−9]
10.0	7.267[−8]	7.439[−9]
11.0	5.859[−8]	5.947[−9]
12.0	4.634[−8]	3.972[−9]
14.0	3.752[−8]	4.166[−9]
16.0	2.804[−8]	3.956[−9]
18.0	2.331[−8]	4.181[−9]

TABLE VI. Absolute errors in the interaction-induced one-electron Darwin correction to the interaction energy of the hydrogen molecule in the $^1\Sigma_g{}^+$ state calculated with the 9/150 and 12/300 basis sets. The symbol $X[\pm n]$ stands for $X \times 10^{\pm n}$.

	9/150			12/300			
R	MC	Exact mon.	CP	MC	Exact mon.	CP	Refs. [51,64]
1.00	5.16[−3]	−8.92[−4]	−3.56[−4]	1.26[−3]	−9.17[−4]	−3.53[−4]	3.25779[−1]
2.00	5.52[−3]	−5.30[−4]	−1.21[−4]	1.65[−3]	−5.20[−4]	−2.25[−5]	2.20827[−2]
4.00	5.57[−3]	−4.83[−4]	−2.00[−5]	1.74[−3]	−4.33[−4]	4.29[−5]	−1.83425[−2]
6.00	5.54[−3]	−5.09[−4]	−2.43[−6]	1.75[−3]	−4.23[−4]	3.72[−6]	−1.64743[−3]
7.00	5.54[−3]	−5.16[−4]	−8.85[−8]	1.72[−3]	−4.53[−4]	3.80[−6]	−4.32567[−4]
8.00	5.54[−3]	−5.09[−4]	−5.18[−7]	1.72[−3]	−4.53[−4]	1.51[−6]	−1.23034[−4]
9.00	5.54[−3]	−5.11[−4]	−2.65[−6]	1.70[−3]	−4.69[−4]	3.70[−7]	−4.13107[−5]
10.0	5.54[−3]	−5.12[−4]	−1.70[−6]	1.71[−3]	−4.60[−4]	−4.28[−7]	−1.69241[−5]
11.0	5.54[−3]	−5.12[−4]	−1.65[−6]	1.70[−3]	−4.70[−4]	−4.10[−7]	−8.30538[−6]
12.0	5.54[−3]	−5.12[−4]	−2.13[−6]	1.70[−3]	−4.69[−4]	−1.12[−7]	−4.57135[−6]

C. Interaction-induced properties

In this section, we apply the counterpoise correction proposed above to calculation of interaction-induced first-order properties defined by Eq. (1). As exemplified by the recent papers devoted to the helium dimer, this task is considerably more challenging than computation of the interaction energy alone [33,34,50]. As a benchmark, we chose as $\hat{X}$ the following operator,

$$\hat{D}_1 = \frac{\pi}{2}\sum_a Z_a \sum_i \delta(\mathbf{r}_{ia}), \tag{29}$$

where Z_a denotes the nuclear charges. The expectation value of the operator $\hat{D}_1$ will be referred to as the one-electron Darwin correction. It appears, e.g., in the relativistic Breit-Pauli theory [65] or in calculation of hyperfine interactions [66]. Because of the singular character of the Dirac distribution $\delta(\mathbf{r})$, the calculation of the expectation value of $\hat{D}_1$ is known to be very demanding and slowly convergent with the size of the Gaussian basis set [40,51].

In Table VI, we show absolute errors in the interaction-induced one-electron Darwin correction for the ground state of H_2. The results obtained with the asymptotic CP method are not shown in this case because they offered no significant improvement over the standard CP. Our results are compared with accurate data of Puchalski *et al.* [64], whenever available ($R \leqslant 10.0$), and the remaining reference values are from Ref. [51]. The error of the results from Refs. [51,64] is negligible in the present context.

The results presented in Table VI show that the counterpoise-corrected method is superior to other techniques in calculation of interaction-induced properties. Similarly, as in the previous case, cf. Table IV, the counterpoise correction gives size-consistent results. In fact, this method is much more effective than in the case of interaction energy calculations, especially at large R. Also, at small R, it performs better than any other scheme. For example, at $R = 1.40$ (basis set 12/300), the errors in the one-electron Darwin correction are about 1.1% and 0.5% with the pure MC method and with subtraction of the exact monomer quantities, respectively. The proposed method reduces this error to less than 0.08%. It appears that the CP method is particularly well suited for calculation of interaction-induced properties with explicitly correlated wave functions.

We close this section by making several observations concerning the computational cost of the proposed scheme. Since in the CP method there is no need to reoptimize the nonlinear parameters in the individual basis functions, the additional task of constructing and diagonalizing the H_0 matrix adds only a relatively small contribution to the total cost of ECG calculations (dominated by massive nonlinear optimizations). Once the optimal supermolecular wave function has been obtained, the corresponding counterpoise-corrected monomer energies become available essentially for free, i.e., at a cost of a single diagonalization for each R. In the asymptotic CP, this cost is reduced only for a single R. We also believe that existing computer programs for explicitly correlated calculations can be modified without significant difficulties to incorporate the proposed scheme.

A possible problem related to the calculation of the counterpoise correction is that the basis set used for the diagonalization of H_0 is usually a few times larger than that used in diagonalizing the dimer Hamiltonian H. This might cause linear dependencies in the basis and, consequently, problems in numerical stability of results. We did not observe this in the calculations presented in this work. This stable behavior is due to the fact that the basis consists of functions adapted to several different representations of the permutation group so the resulting overlap matrix is block diagonal. One should note, however, that the H_0 matrix is not only larger, but also formulas for its matrix elements are somewhat more complicated than in the case of the dimer Hamiltonian (H_0 does not commute with all permutations and some of them cannot be moved to only one side of the bracket).

IV. CONCLUSIONS

In this work, we have presented a technique, analogous to the counterpoise correction in the Boys-Bernardi scheme, to restore size consistency and eliminate basis set superposition error in explicitly correlated electronic structure calculations. This method is based on relaxing the Pauli principle in computation of the expectation value of the sum of monomer Hamiltonians (or other monomer property operators). This leads to distance-dependent monomer energies and/or properties corresponding to the given supermolecular basis set and monomer spin states. It has been shown that the proposed method yields interaction energies and interaction-induced properties which vanish at large intermonomer separations.

We would like to stress that the proposed method does *not* provide a way to construct individual basis sets for the monomers from a given supermolecular basis set. Similarly, the presented method does not allow us to calculate contributions to Eq. (1) coming from individual monomers but only the sum of monomer quantities.

Exemplary ECG calculations for the hydrogen molecule (H_2) indicate that the counterpoise correction significantly improves the quality of the results, especially in the long-range regions of the potential energy curve. This is true for the interaction energies, but especially for a more challenging case of first-order interaction-induced properties (one-electron Darwin correction has been tested). The additional computational cost of the proposed scheme is small compared to the necessary optimizations of the supermolecular wave function.

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