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

Michal Lesiuk* and Bogumil Jeziorski
Faculty of Chemistry, University of Warsaw
Pasteura 1, 02-093 Warsaw, Poland
(Dated: December 21, 2018)

Explicitly correlated calculations of interaction energies with wave functions that include all inter-particle distances have suffered so far from the lack of size-consistency resulting from the difficulty to define 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 communication 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.

PACS numbers: 31.15.vn, 03.65.Ge, 02.30.Gp, 02.30.Hq

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

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

(1)

for a system described by the wave function $\psi$, and composed of two subsystems (monomers $A$, $B$) with the wave functions $\psi_A$, $\psi_B$. The operators $\hat{X}_A$ and $\hat{X}_B$ are defined analogously to $\hat{X}$, but involve summations only over 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, $\Delta X$, 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 $\Delta X$ 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 $\Delta X$ rely on the supermolecular approach since the standard electronic structure methods are unable to yield the difference $\Delta X$ 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 $\Delta X$ can be several orders of magnitude smaller than the subtracted terms on the right-hand-side of Eq. (1). In practice, $\Delta X$ 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 $\Delta X$. 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

* e-mail: lesiuk@tiger.chem.uw.edu.pl
superposition error (BSSE), cannot be viewed as a legitimate part of the interaction energy. In calculations employing one-electron basis sets (algebraic approximation) 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 [27–29], 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 a 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 $\Delta X$ 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 non-adiabatic Schrödinger equation for few-body systems [30, 31]. 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 [32–41], by any other method. It should be stressed, however, that the method proposed by us can also be applied to calculations with Slater geminals [42–45], Hylleraas CI expansions [46–48], and other multi-electron 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 $\Delta X$. This brute-force approach typically works well for separations where $\Delta X$ is much larger than the error in $\langle \psi | X | \psi \rangle$. However, it does nothing to restore the size-consistency. As $\Delta X$ 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. [49, 50].

Another strategy, called the monomer-contraction (MC) method, has been proposed by Cencek et al. [34, 35, 51]. The main idea of this method is to build the product of the best available monomer wave functions into the dimer basis and represent $\psi$ as

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

where $\psi_A, \psi_B$ are wave functions optimized separately for monomers $A$ and $B$, and fixed during the calculations for the dimer, $\Pi$ is a projection operator ensuring that $\psi$ has the correct permutation and spatial symmetry, and $\phi_k$ 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 $\phi_k$ is directed mostly towards the interaction-induced part of the dimer wave function. The monomer quantities entering Eq. (1) can be computed from $\psi_A, \psi_B$ 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 [41].

A different approach to solve the size-consistency problem in the ECG method was proposed by Piszczatowski et al. [52]. In this approach, related to SAPT but not relying on the convergence of a perturbation expansion, the difference $\Delta X$ 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 $\Delta X$ 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 $\psi, \psi_A$, and $\psi_B$, employed in Eq. (1) to compute $\Delta X$, 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

\[
\phi = \prod_{i=1}^{N} e^{-\alpha_i |r_i - a|^2} \prod_{i=1}^{N} e^{-\beta_i |r_i - b|^2} \prod_{i,j=1}^{N} e^{-\gamma_{ij} |r_i - r_j|^2}, \tag{3}
\]

where \( r_i, i = 1, \ldots, N, \) are vectors containing Cartesian coordinates of electrons, \( a \) and \( b \) are vectors specifying the nuclear positions, \( R = |a - b|, \) and \( N = N_A + N_B. \) The exponents \( \alpha_i, \beta_j, \) and \( \gamma_{ij} \) 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 \( \Sigma^+ \) state. The functions of the form of Eq. (3) constitute a potentially complete basis set in the space of \( \Sigma^+ \) symmetry [53, 54]. To construct ECGs of other symmetries one can follow the prescription of Ref. [53]. 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 \( e^{-\beta_i |r_i - b|^2} \) \( (e^{-\alpha_i |r_i - a|^2}) \) are eliminated.

We assume that the Hamiltonians \( \hat{H}, \hat{H}_A, \) and \( \hat{H}_B \) are non-relativistic 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 [55-57]. 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 \([2^{N/2-S} \times 1^2S]\). This symmetry of the wave function can be enforced with the help of appropriate Young operators [57]. Within the present computational capabilities this spin-free ECG method is applicable to systems containing up to seven/eight active particles, see Refs. [58, 59] 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 \( \psi \) and \( \psi_A \) or \( \psi_B \) 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 non-degenerate. The functions \( \psi \) and \( \psi_0 \) 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 \( \Delta X \) to correctly vanish at large separations.

The problem with this idea is that \( \psi \) and \( \psi_0 \) have different symmetries and, even at large \( R, \) reside in distant locations of the Hilbert space [60]. This is a consequence of the fact that \( \hat{H} \) and \( \hat{H}_0 \) have different symmetry groups, denoted by \( G \) and \( G_0 \) further in the text. It is impossible to perform calculations for \( \psi \) and \( \psi_0 \) in a common basis adapted to irreducible representations of both \( G \) and \( G_0. \) The main idea of our method is to perform calculations with the basis that is adapted to \( G \cap G_0, \) i.e., the largest subgroup of \( G \) and \( G_0. \) To guarantee that \( \psi \) is a pure spin state we also impose the condition that this basis is invariant under all operations of \( G. \)

To illustrate this idea with a simple example we assume that \( A \) and \( B \) are ground-state hydrogen atoms. In this case \( G = \mathbb{D}_{\infty h} \times S_2 \) and \( G_0 = O_a(3) \times O_b(3) \times G_1, \) where \( O_a(3) \) and \( O_b(3) \) are symmetry groups of \( H_A \) and \( H_B, \) respectively, and \( G_1 = \{ E, P^+ \} \) is the two-element group containing the identity element \( E \) and the permutation-inversion operation \( P^+ = IP_{12}. \) The latter is a combination of the inversion \( I \) with respect to the center of the diatom and the transposition \( P_{12} \) of the coordinates of the \( i \)th and \( j \)th electron. The groups \( O_a(3) \) and \( O_b(3) \) contain all rotations and the inversion with respect to the respective nuclear positions \( a \) and \( b \) (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 \( G \) and \( G_0 \) is the group \( C_{uv} \times G_1. \) The primitive ECG function of Eq. (3) is already adapted to \( C_{uv}. \) To additionally adapt this basis to \( G_1 \) we project it with \( (1 + P^+) / 2 \) (we take the plus sign in the projector since both \( \psi_0 \) and \( \psi \) are symmetric under the action of \( P^+ \)). The basis adapted to \( G \cap G_0 \) consists thus of functions of the form

\[
\phi' = e^{-\alpha_1 r_{i1}^2} e^{-\alpha_2 r_{i1}^2} e^{-\beta_1 r_{i2}^2} e^{-\beta_2 r_{i2}^2} e^{-\gamma_0 r_{i1}^2} + e^{-\beta_2 r_{i1}^2} e^{-\beta_1 r_{i2}^2} e^{-\alpha_2 r_{i2}^2} e^{-\gamma_0 r_{i1}^2}, \tag{6}
\]

where \( r_{ai} = |r_i - a|, \) \( r_{bi} = |r_i - b|, \) and \( r_{ij} = |r_i - r_j|. \) This basis is not invariant under the operations of \( G, \) so we have to augment it by adding functions \( I \phi' \) and \( P_{12} \phi'. \) Both augmentations lead to the same result so the final basis consists of functions of the form of \( \phi' \) and \( P_{12} \phi'. \) In Section 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 en-
energy approaches zero at infinity. In practice it is useful to follow the idea of the monomer-contraction method [34, 35, 51] and extend this basis by two additional functions: \( \tilde{\psi}_A \psi_B \) 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 \( \psi_B = P^* \tilde{\psi}_A \). These two basis functions are fixed and, unlike all functions of the form \( \phi' \) 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 the dimer symmetry group \( G \). If one is interested in the triplet \( ^3\Sigma^+ \) state then the size of the basis can be reduced by the factor of two 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 \( P_{12} \) (triplet functions) but are also ungerade under the action of the inversion operator \( I \) since \( I \phi' = P_{12} \phi' \) and, consequently,

\[
\hat{I} (1 - P_{12}) \phi' = -(1 - \hat{I}) \phi' = -(1 - P_{12}) \phi'.
\]  

(7)

It is easy to verify that Eq. (7) holds also when \( \phi' \) is replaced by \( \tilde{\psi}_A \psi_B \) and that the singlet functions obtained by the symmetrization \( 1 + P_{12} \) have gerade symmetry, i.e., are invariant under the inversion \( I \). 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 \( \psi_0 \) 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 \( \phi' \) and \( P_{12} \phi' \).

When the interacting one-electron systems are different, as in the case of \( \text{He}^+ \cdots \text{H} \) interaction, \( G = C_{\infty v} \times S_2 \), \( G_0 = O_a (3) \times O_b (3) \), and \( G \cap G_0 = C_{\infty v} \). The inversion symmetry is not present and the basis for the monomer calculations is constructed from the functions \( \psi \) and \( P_{12} \psi \), where \( \psi \) is the two-electron primitive ECG [given by the first term on the r.h.s. 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 due to the multidimensionality of the representations of the permutation group. The dimer group \( G \) contains now the factor \( S_N \) instead of \( S_2 \) and one has to include in \( G_0 \) the product \( S_N \times S_{N} \times S_{\infty v} \) of the monomer permutation groups. Similarly 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 \( \Gamma_0 \) of \( G \cap G_0 \). Next, one forms the basis of the induced representation \( \Gamma \uparrow G \) and takes the functions adapted simultaneously to \( \Gamma_0 \) and to the irreducible representations of \( G \) entering \( \Gamma_0 \uparrow G \). 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 \( G = C_{\infty v} \times S_3 \), while \( G_0 = O_a (3) \times O_b (3) \times S_2 \), and \( G \cap G_0 = C_{\infty v} \times S_2 \). For the singlet state of helium the function \( \psi_0 = \psi_{1e} \psi_{1h} \) is symmetric and the molecular \( ^2 \Sigma^+ \) function can be chosen to be symmetric under the permutation \( P_{12} \). Therefore, we can symmetrize the ECG basis and consider further the functions \( \phi' = (1 + P_{12}) \phi \), where \( \phi \) is a primitive, three-electron, two-center ECG function of the form of Eq. (3). To obtain the basis invariant under the action of \( S_3 \) we have to perform the induction process, i.e., act on \( \phi' \) with all permutations from \( S_3 \). In this way we obtain three ECG functions \( \phi', P_{13} \phi', \) and \( P_{23} \phi' \) forming a basis for the induced representation \( [2] \uparrow S_3 \). The representation \( [2] \uparrow S_3 \), referred also as the outer product \([2] \otimes [1]\) (see Ref. [57]), is reducible and decomposes as

\[
[2] \uparrow S_3 = [21] + [3],
\]

(8)

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

\[
\begin{array}{c}
\begin{array}{c}
\text{O} \\
\end{array}
\end{array} \otimes \begin{array}{c}
\begin{array}{c}
\text{O} \\
\end{array}
\end{array} = \begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\end{array}.
\]

(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

\[
\phi'' = (2 - P_{13} - P_{23}) \phi'
\]

(10)

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

\[
\phi''' = (1 + P_{13} + P_{23}) \phi'
\]

(11)

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

\[
\omega^{[N]}_{rt'} = \sum_{P \in S_N} \Gamma_{rt'}^{[N]}(P) P,
\]

(12)

where \( \Gamma_{rt'}^{[N]}(P) \) are matrices of the representation \([N]\) \([57]\). Since the nonlinear parameters are optimized only for the dimer, these parameters are identical in \( \phi'' \) and \( \phi''' \). 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. [55, 56], 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 $S_2$ factor in $\mathcal{G}$ is replaced by $S_4$, and the $S_2$ factor in $\mathcal{G}_0$ by $S_4$. The doublet states of lithium exhibit (unphysical) exchange degeneracy since the $[21]$ representation is two dimensional and we have two standard Young tableaux
\[ \begin{array}{c}
| & | \\
| & | \\
\end{array} \quad \text{and} \quad \begin{array}{c}
| & | \\
| & | \\
\end{array}. \quad (13)
\]

We (arbitrarily) choose the first one and require that the lithium wave function $\psi_{11}$ as well as the molecular function $\psi_{L_{1H}}$ are 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 one can show that the space spanned by
\[ (3 + P_{14})(1 + P_{14} + P_{24}) \phi', \]
\[ (1 + P_{14})(1 - P_{14} - P_{24}) \phi', \]
\[ (1 - P_{14})(3 - P_{14} - P_{24}) \phi'. \]

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: $\mathcal{G} = D_{\infty h} \times S_4$, $\mathcal{G}_0 = O_h(3) \times O_b(3) \times S_2 \times S_2 \times G_1$, and $\mathcal{G} \cap \mathcal{G}_0 = C_{\infty v} \times S_2 \times S_2 \times \mathcal{G}_f$, where $\mathcal{G}_f = \{ E, \hat{I} P_{ab} \}$ 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 $P_{13} P_{24}$, $P_{14} P_{23}$, $P_{32} P_{41}$, or $P_{43} P_{12}$ without changing the $S_2 \times S_2 \times \mathcal{G}_f$ 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
\[ \phi' = (1 + P_{13})(1 + P_{34})(1 + \hat{I} P_{ab}) \phi, \]
where $\phi$ is the primitive ECG function of Eq. (3) with $N = 4$. Performing the induction of the fully symmetric representation of $S_2 \times S_2$ to $S_4$ one finds
\[ [2] \times [2] \uparrow S_4 = [4] + [31] + [22], \]
which can be written by using the Young diagrams as
\[ \begin{array}{c|c|c}
| & | & | \\
| & | & | \\
\end{array} \begin{array}{c|c|c}
| & | & | \\
| & | & | \\
\end{array} = \begin{array}{c|c|c|c}
| & | & | & | \\
| & | & | & | \\
\end{array} + \begin{array}{c|c|c|c}
| & | & | & | \\
| & | & | & | \\
\end{array} + \begin{array}{c|c|c|c}
| & | & | & | \\
| & | & | & | \\
\end{array}. \quad (22)
\]

The induction from $C_{\infty v}$ to $D_{\infty h}$ is not needed since one can show that the space spanned by $P \phi'$, $P \in S_4$ is invariant under the inversion $\hat{I}$. The induced representation $[2] \times [2] \uparrow S_4$ is six-dimensional but, since we can work only with functions fully symmetric under $S_2 \times S_2$, only three functions are necessary
\[ \phi^{[4]} = (1 + P_{13} P_{24} + P_{14} + P_{23} + P_{24}) \phi', \]
\[ \phi^{[31]} = (1 - P_{13} P_{24}) \phi', \]
\[ \phi^{[22]} = (2 + 2 P_{13} P_{24} - P_{14} - P_{23} - P_{24}) \phi'. \]

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
\[ \hat{I} \phi' = P_{ab} \phi', \]
for any of the four permutations $P_{ab}$. One can show that the parts of $\phi^{[4]}$ or $\phi^{[31]}$ generated by $1 + P_{13} P_{24}$, $P_{13}$ and $P_{24}$, and by $P_{23} + P_{14}$ are separately invariant under the action of $\hat{I}$. Specifically
\[ \hat{I}(P_{13} + P_{24}) \phi' = \hat{I} \phi' = (P_{13} + P_{24}) P_{13} P_{24} \phi' = (P_{13} + P_{24}) \phi', \]
\[ \hat{I}(P_{23} + P_{14}) \phi' = \hat{I} \phi' = (P_{23} + P_{14}) P_{23} P_{14} \phi' = (P_{23} + P_{14}) \phi', \]
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
we present absolute monomer energies calculated from the MC functional and demonstrate that the dimer energy appears two times in the direct product [21]. Technical details of this procedure can be found, for example, in Refs. [62, 63]. About one thousand optimization sweeps over the whole basis set were performed for each internuclear distance. The 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.

### 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

$$(1 + P_{12})(1 + P_{ab})\left[\phi_0 \phi_1(s_{1a}) \phi_1(s_{2b}) + \sum_{k=1}^{K} c_k \phi_k\right],$$

(27)

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

$$\phi_k = e^{-a_kr_{1a}^2 - b_kr_{1b}^2 - c_kr_{2a}^2 - d_kr_{2b}^2 - w_kr_{12}^2},$$

(28)

and $\phi_1(s)$ is the hydrogenic 1$s$ orbital expanded as a linear combination of Gaussian 1$s$ 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 non-linear 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 [61].

Technical details of this procedure can be found, for example, in Refs. [62, 63]. About one thousand optimization sweeps over the whole basis set were performed for each internuclear distance. The 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.

#### 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 ($^2\Sigma^+_g$) 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.

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 [64] 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 func-

| Molecular State | Energy E (a.u.) | Error (a.u.) |
|----------------|----------------|--------------|
| $^1\Sigma^+_g$ | $-0.499\,999\,904$ | $0.000\,000\,096$ |

**Table I. Properties of the hydrogen atom calculated with the orbital 1$s$ expanded in 9 or 12 primitive Gaussian functions.** $E$ is the electronic energy and $\langle\delta(r)\rangle$ is the expectation value of delta distribution centered at the nucleus. Errors with respect to the exact values are given below each entry.
Dimer energy and the counterpoise corrected energy of noninteracting atoms for the hydrogen molecule \((\text{H}_2)\) in the \(^1\Sigma^+_u\) 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 \(X \cdot 10^n\).

| \(R\) | 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} |

Molecule energy and the counterpoise corrected energy of noninteracting atoms for the HeH molecule in the lowest \(^2\Sigma^+_u\) 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 \(X \cdot 10^n\).

| \(R\) | 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} |

Optimization is biased towards 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 it 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 an 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 – similarly 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

\(\sum_{\text{interatomic distance}}\). 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

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 non-zero 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 \(R \to \infty\).

For larger systems) gives better results than the CP correction. However, quite remarkably, the asymptotic CP method gives uniformly very good results for all interatomic distances, always better than the subtraction of the exact monomer energies.

It is obvious that the relative errors in the interaction energies computed using the MC method or the exact monomer 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 (not increasing to infinity at large \(R\)). 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

\[\sum R_{\text{dimer energy}} = 1\]
show that the

Ⅴ

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

−

-
terpoise 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 re-optimize 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 they cannot be moved to only one side of the bracket).

\section*{IV. CONCLUSIONS}

In this work we have presented a novel 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. The new 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/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 \textit{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 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.

\begin{table}[h]
\centering
\caption{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 $X \cdot 10^n$.}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
 & \multicolumn{3}{|c|}{9/150} & \multicolumn{3}{|c|}{12/300} \\
\hline
$R$ & MC & exact mon. & CP & MC & exact mon. & CP \\
\hline
1.00 & 5.16_{-3} & -8.92_{-4} & -3.56_{-4} & 1.26_{-3} & -9.17_{-4} & -3.53_{-4} \\
2.00 & 5.52_{-3} & -5.30_{-4} & -1.21_{-4} & 1.65_{-3} & -5.20_{-4} & -2.25_{-5} \\
4.00 & 5.57_{-3} & -4.83_{-4} & -2.00_{-5} & 1.74_{-3} & -4.33_{-4} & -4.29_{-5} \\
6.00 & 5.54_{-3} & -5.09_{-4} & -2.43_{-5} & 1.75_{-3} & -4.23_{-4} & -3.72_{-5} \\
7.00 & 5.54_{-3} & -5.16_{-4} & -8.85_{-5} & 1.72_{-3} & -4.53_{-4} & -3.80_{-6} \\
8.00 & 5.54_{-3} & -5.09_{-4} & -5.18_{-5} & 1.72_{-3} & -4.53_{-4} & -1.51_{-6} \\
9.00 & 5.54_{-3} & -5.11_{-4} & -2.65_{-6} & 1.70_{-3} & -4.69_{-4} & -3.70_{-6} \\
10.0 & 5.54_{-3} & -5.12_{-4} & -1.70_{-6} & 1.71_{-3} & -4.60_{-4} & -4.28_{-6} \\
11.0 & 5.54_{-3} & -5.12_{-4} & -1.65_{-6} & 1.70_{-3} & -4.70_{-4} & -4.10_{-7} \\
12.0 & 5.54_{-3} & -5.12_{-4} & -2.13_{-6} & 1.70_{-3} & -4.69_{-4} & -1.12_{-7} \\
\hline
\end{tabular}
\end{table}
ACKNOWLEDGMENTS

This work was supported by the National Science Center, Poland within the project 2017/27/B/ST4/02739. The authors are grateful to Jacek Komasa for making his ECG program available to us.

[1] B. Jeziorski, R. Moszynski, and K. Szalewicz, Chem. Rev. 94, 1887 (1994).
[2] E. G. Hohenstein and C. D. Sherrill, WIREs Comput. Mol. Sci. 2, 304 (2011).
[3] K. Szalewicz, WIREs Comput. Mol. Sci. 2, 254 (2012).
[4] G. Jansen, WIREs Comput. Mol. Sci. 4, 127 (2014).
[5] R. J. Bartlett, Ann. Rev. Phys Chem. 32, 359 (1981).
[6] R. J. Bartlett and M. Musial, Rev. Mod. Phys. 79, 291 (2007).
[7] E. Clementi, J. Chem. Phys. 46, 3851 (1967).
[8] N. R. Kestner, J. Chem. Phys 48, 252 (1968).
[9] H. Jansen and P. Ros, Chem. Phys. Lett. 3, 140 (1969).
[10] S. Boys and F. Bernardi, Mol. Phys. 19, 553 (1970).
[11] B. Liu and A. D. McLean, J. Chem. Phys. 59, 4557 (1973).
[12] M. Gutowski, F. V. Duijneveldt, G. Chałasiński, and L. Piela, Chem. Phys. Lett. 129, 325 (1986).
[13] M. Gutowski, F. B. V. Duijneveldt, G. Chałasiński, and L. Piela, Mol. Phys. 61, 233 (1987).
[14] G. Chałasiński and M. Gutowski, Chem. Rev. 88, 943 (1988).
[15] M. Gutowski, J. G. C. M. van Duijneveldtvan de Rijdt, J. H. van Lenthe, and F. B. van Duijneveldt, J. Chem. Phys. 98, 4728 (1993).
[16] E. R. Davidson and S. J. Chakravorty, Chem. Phys. Lett. 217, 48 (1994).
[17] M. Gutowski, M. M. Szczesniak, and G. Chałasiński, Chem. Phys. Lett. 241, 140 (1995).
[18] G. Chałasiński and M. M. Szczesniak, Chem. Rev. 100, 4227 (2000).
[19] J. H. Van Lenthe, J. G. C. M. Duijneveldt-Van Devan Rijdt, and F. B. Van Duijneveldt, “Weakly bonded systems,” in Adv. Chem. Phys. (Wiley-Blackwell, 2007) pp. 521–566.
[20] N. R. Kestner and J. E. Combariza, “Basis set superposition errors: Theory and practice,” in Reviews in Computational Chemistry (Wiley-Blackwell, 2007) pp. 99–132.
[21] L. M. Mentel and E. J. Baerends, J. Chem. Theory Comput. 10, 252 (2014).
[22] S. Simon, M. Duran, and J. J. Dannenberg, J. Chem. Phys. 105, 11024 (2000).
[23] S. S. Xanthas, J. Chem. Phys 104, 8821 (1996).
[24] K. Szalewicz and B. Jeziorski, J. Chem. Phys 109, 1198 (1998).
[25] K. R. Liedl, J. Chem. Phys. 108, 3199 (1998).
[26] T. H. Dunning, J. Phys. Chem. A 104, 9062 (2000).
[27] T. V. Mourik, A. K. Wilson, K. A. Peterson, D. E. Woon, and T. H. Dunning (Academic Press, 1998) pp. 105 – 135.
[28] A. Halkier, W. Klopper, T. Helgaker, P. Jørgensen, and P. R. Taylor, J. Chem. Phys. 111, 9157 (1999).
[29] A. J. C. Varandas, J. Phys. Chem. A 114, 8505 (2010).
[30] S. Bubin, M. Pavanello, W.-C. Tung, K. L. Sharkey, and L. Adamowicz, Chem. Rev. 113, 36 (2013).
[31] J. Mitroy, S. Bubin, W. Horiiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, Rev. Mod. Phys. 85, 693 (2013).
[32] K. Pachucki and J. Komasa, Phys. Rev. Lett. 92, 213001 (2004).
[33] M. Puchalski, J. Komasa, and K. Pachucki, Phys. Rev. A 92, 062501 (2015).
[34] W. Cencek, J. Komasa, K. Pachucki, and K. Szalewicz, Phys. Rev. Lett. 95, 233004 (2005).
[35] W. Cencek and K. Szalewicz, Int. J. Quantum Chem. 108, 2191 (2008).
[36] S. Bubin and L. Adamowicz, J. Chem. Phys. 135, 244104 (2011).
[37] W.-C. Tung, M. Pavanello, and L. Adamowicz, J. Chem. Phys. 134, 064117 (2011).
[38] L. Adamowicz and M. Pavanello, Philos. Trans. Royal Soc. A 370, 5001 (2012).
[39] M. Puchalski, J. Komasa, and K. Pachucki, Phys. Rev. A 87, 030502 (2013).
[40] E. Mátyus, T. Szidarovszky, and A. G. Császár, J. Chem. Phys. 141, 154111 (2014).
[41] M. Przybytek, W. Cencek, B. Jeziorski, and K. Szalewicz, Phys. Rev. Lett. 119, 123401 (2017).
[42] A. J. Thakkar and V. H. Smith, Phys. Rev. A 15, 1 (1977).
[43] A. M. Frolov and V. H. S. Jr, J. Phys. B: At. Mol. Opt. Phys. 28, L449 (1995).
[44] V. I. Korobov, Phys. Rev. A 66, 024501 (2002).
[45] M. Puchalski and K. Pachucki, Phys. Rev. A 81, 052505 (2010).
[46] J. S. Sims and S. A. Hagstrom, Phys. Rev. A 4, 908 (1971).
[47] J. S. Sims and S. A. Hagstrom, J. Chem. Phys. 55, 4699 (1971).
[48] J. S. Sims and S. A. Hagstrom, Int. J. Quantum Chem. 9, 149.
[49] J. Rychlewski, W. Cencek, and J. Komasa, Chem. Phys. Lett. 229, 657 (1994).
[50] W. Cencek, J. Komasa, and J. Rychlewski, Chem. Phys. Lett. 246, 417 (1995).
[51] K. Patkowski, W. Cencek, P. Jankowski, K. Szalewicz, J. B. Mehl, G. Garberoglio, and A. H. Harvey, J. Chem. Phys. 129, 094304 (2008).
[52] K. Piszczatowski, G. Lach, and B. Jeziorski, Phys. Rev. A 77, 062514 (2008).
[53] B. Jeziorski, R. Bukowski, and K. Szalewicz, Int. J. Quantum Chem. 61, 769 (2007).
[54] R. N. Hill, Int. J. Quantum Chem. 68, 357 (2008).
[55] K. Patkowski, T. Korona, and B. Jeziorski, J. Chem. Phys. 115, 1137 (2001).
[56] K. Patkowski, B. Jeziorski, T. Korona, and K. Szalewicz, J. Chem. Phys 117, 5124 (2002).
[57] I. G. Kaplan, The Pauli Exclusion Principle: Origin, Verifications, and Applications (Wiley, Chichester, 2017).
[58] S. Bubin, M. Stanke, and L. Adamowicz, J. Chem. Phys. 131, 044128 (2009).
[59] K. L. Sharkey and L. Adamowicz, J. Chem. Phys. 140, 174112 (2014).
[60] B. Jeziorski and W. Kołos, Int. J. Quantum Chem., Suppl. 1 12, 91 (1977).
[61] M. J. D. Powell, Comput. J. 7, 155 (1964).
[62] J. Komasa and A. J. Thakkar, Mol. Phys. 78, 1039 (1993).
[63] J. Komasa, Phys. Rev. A 65, 012506 (2001).
[64] K. Pachucki, Phys. Rev. A 82, 032509 (2010).
[65] M. Puchalski, J. Komasa, and K. Pachucki, Phys. Rev. A 95, 052506 (2017).
[66] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two- Electron Systems (Springer: Berlin, 1975).
[67] K. Pachucki and J. Komasa, Phys. Rev. A 83, 042510 (2011).