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**REGULAR ARTICLE**

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# An extended group function model for intermolecular interactions

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**Abstract** An extended group function model is introduced for the calculation of intermolecular interactions. The model is formulated within the framework of the energy incremental scheme. In the calculation of intra- and intersystem energies, model systems are introduced. To each subsystem is associated a set of partner subsystems defined by a vicinity criterion. In the independent calculation of intra- and intersystem energies, calculations are performed on model systems defined by the subsystems considered and their partner subsystems. To further reduce computation time, dual basis sets are introduced. A small and a large basis set are associated with each subsystem. For partner subsystems in a model system, the small basis set is adopted. Test calculations are performed on helium atoms in one- and two-dimensional lattices.

## 1 Introduction

Intermolecular interactions govern the behaviour of matter in bulk from gas imperfections, molecular scattering cross-sections and transport properties of gases to the liquid and the solid state. Prediction and explanations are based on the concept of the intermolecular potential energy surface (PES) which is defined in the context of quantum mechanics, As for ab initio calculations of PES, nowadays, it is possible to obtain reliable PES for small clusters comprising closed shell species [1]. However, there are exceptions. The calculation of the binding energy of the beryllium dimer, a very small molecule, is still a difficult task for most of the conventional models in this field [2]. If we consider larger systems, new methodological developments are required in order to obtain a practical ab initio tool which can be applied for these systems.

Intermolecular binding energies are usually one or two orders of magnitude smaller than the binding energy associated with a covalent bond. Hence, a computational model aimed at describing intermolecular interactions is subjected to very strict requirements. The following ones are of particular importance:

*Conceptual requirements* The model should have a conceptual structure which facilitates interpretation, i.e. concepts which help to illustrate the physical mechanism of the phenomenon under study. By understanding the mechanism involved, it is also easier to see how a mathematical model should be refined, in order to get an improved description of the problem in question.

*Application for any intersystem distances* In order to avoid spurious results, the same model should be applicable for the whole region of configuration space.

*Size extensivity* A model is size-extensive if, for two non-interacting systems $A$ and $B$, the calculated energy satisfies the relation

$$E(A \cdots B) = E(A) + E(B) \tag{1}$$

where $E(A \cdots B)$ is the calculated energy when $A$ and $B$ are considered as a combined system, and $E(A)$ and $E(B)$ are the energies of $A$ and $B$, respectively, when they are treated as separate systems. This property is of paramount importance for large systems, but even for small systems like the dimers of helium and hydrogen, it is essential.

*Avoidance of basis set artefacts* Any molecular calculation is based on an incomplete one-electron basis. This influences the calculated result in two ways. First, the basis set might not be sufficiently flexible to describe the changes taking place during the formation of the complex, and the calculated energy will be too high. On the other hand, basis functions which are centred on the nuclei of one subsystem, will in a supersystem calculation improve the intrasystem part of the wave functions corresponding to another subsystem. This second effect, denoted the basis set superposition error (BSSE), yields an artificial lowering of the energy of the supersystem. A reliable approach requires that these effects be controlled individually.

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*Computational feasibility* In order to be useful as a tool for predicting or explaining properties related to intermolecular interactions, a model has to perform well along this dimension.

There are two main classes for the calculation of intermolecular potentials: methods which are based on considering the interaction between the subsystems as a perturbation, and the supermolecule approach where the interacting subsystems are considered as a supermolecule. A description of these different approaches may be found in the monographs of Maitland et al. [3], Hobza and Zahradnik [4], and Stone [5]. The model to be advocated in this work is within the supermolecule framework.

The purpose of the present work is to construct a computational model for large complexes comprising small subsystems, and where the accuracy of the calculation is close to the accuracy of a calculation on a dimer comprising any pair of subsystems for the complex.

The structure of the paper is as follows. Section 2 is devoted to the theoretical framework. In sect. 3, we introduce the numerical models. Section 4 presents test calculations on extended linear and planar complexes of helium.

## 2 The theoretical framework

### 2.1 The energy incremental method

The computational paradigm is the energy incremental method. It was first introduced by Nesbet when he considered the hierarchy of the Bethe–Goldstone equations [6]. According to Nesbet the full configuration interaction (FCI) correlation energy for an $N$-electron system can be written as

$$E_{\text{corr}}^{\text{FCI}} = \sum_{i=1}^{N} e_i + \sum_{i<j}^{N} e_{ij} + \sum_{i<j<k}^{N} e_{ijk} + \cdots + e_{12\ldots N} \tag{2}$$

In Eq. (2), the indices $i,\ j,\ k, \ldots$ refer to occupied spin orbitals of a Slater determinant. In this hierarchy, the basic unit is a spin orbital. The determination of the corrections $\{e_i\}$, $\{e_{ij}\}$, $\{e_{ijk}\}, \ldots$ are based on partial variational calculations.

Røeggen [7] introduced the extended geminal model for a closed shell $2N$-electron system. This model is also based on the energy incremental method. However, the basic unit is not a spin orbital but a two-electron wave function – a geminal – associated with each electron pair. The geminals are singlet-coupled. The energy is in this case

$$\begin{aligned} E^{\text{FCI}} = E^{\text{APSG}} &+ \sum_{K=1}^{N} \epsilon_K + \sum_{K<L}^{N} \epsilon_{KL} \\ &+ \sum_{K<L<M}^{N} \epsilon_{KLM} + \cdots + \epsilon_{12\ldots N} \end{aligned} \tag{3}$$

where $E^{\text{APSG}}$ is the energy associated with the basic approximation which is an antisymmetric product of strongly orthogonal geminals (APSG). The summations in Eq. (3) are over geminals. If all the geminals in the APSG wave function are defined in terms of only one spatial orbital, i.e. the APSG function is a restricted Hartree–Fock (RHF) wave function, then the sum of the correction terms in Eq. (3) is the FCI correlation energy. The energy incremental scheme introduced by Stoll [8] is identical to an extended geminal approach based on RHF geminals.

The feasibility and the accuracy of the energy incremental method have been demonstrated in a large number of works by Stoll and coworkers. The method has been applied to insulators [9,10], semiconductors [11,12], rare-gas crystals [13], polymers [14], graphite [15], and very recently to a calculation on the buckminsterfullerene $C_{60}$ [16]. Røeggen [17] and coworkers have used extended geminal models to calculate the interatomic or intermolecular potential for several complexes. References to these works can be found in the review article on extended geminal models.

### 2.2 An extended group function model

On the basis of the extended geminal expansion, Eq. (3), Røeggen et al. [18] introduced an extended group function (EXGF) model. Their model is utilized in this work. Proper geminals, i.e. each geminal is defined in terms of more than one spatial orbital, have a localized character as a result of the optimization of the APSG function. If the basic approximation is an RHF function, which is assumed in this work, the orbitals are localized. We have previously advocated a minimal distortion localization scheme [2,19]. The localized supersystem orbitals are obtained by minimizing a least-square deviation from the isolated subsystem orbitals. Then the nuclei and the electron pairs (orbitals) localized in the same part of the physical space define the subsystems. We assume that our complex consists of $n$ interacting subsystems and subsystem number $s$ comprises $N_s$ electron pairs. A simple reordering of the terms in Eq. (3) yields

$$\begin{aligned} E^{\text{EXGF}} = E^{\text{RHF}} &+ \sum_{s=1}^{n} \left\{ \sum_{K=1}^{N_s} \epsilon_{s,K} \right. \\ &\left. + \sum_{K_1<K_2}^{N_s} \epsilon_{s,K_1K_2} + \cdots + \epsilon_{s,12\ldots N_s} \right\} \\ &+ \sum_{s<t}^{n} \left\{ \sum_{K=1}^{N_s} \sum_{L=1}^{N_t} \epsilon_{s,K;t,L} + \sum_{K_1<K_2}^{N_s} \sum_{L=1}^{N_t} \epsilon_{s,K_1K_2;t,L} \right. \\ &\left. + \sum_{K=1}^{N_s} \sum_{L_1<L_2}^{N_t} \epsilon_{s,K;t,L_1L_2} + \cdots \right\} \\ &+ \sum_{s<t<u}^{n} \left\{ \sum_{K=1}^{N_s} \sum_{L=1}^{N_t} \sum_{M=1}^{N_u} \epsilon_{s,K;t,L;u,M} + \cdots \right\} + \cdots \end{aligned} \tag{4}$$

The particular way the terms are grouped in Eq. (4) leads naturally to a simple expression for the energy

$$E^{\mathrm{EXGF}} = E^{\mathrm{RHF}} + \sum_{s=1}^{n} E^{s}_{\mathrm{corr}} + \sum_{s<t}^{n} E^{s,t}_{\mathrm{corr}} + \sum_{s<t<u}^{n} E^{s,t,u}_{\mathrm{corr}} + \cdots \tag{5}$$

The definition of the terms in Eq. (5) should be obvious. However, we can reinterpret the terms in Eq. (5). The term $E^{s}_{\mathrm{corr}}$, which we might denote a one-body correlation term, is simply the correlation energy for subsystem $s$. In principle, it is obtained by an FCI calculation on subsystem number $s$ when the residual subsystems are described by an RHF approximation. Similarly, the two-body correlation term, $E^{s,t}_{\mathrm{corr}}$, is the intersystem correlation energy for $s$ and $t$ when the residual subsystems are described by an RHF approximation. It is identical to the difference between the FCI energy correction for the composite system $s+t$ in the supersystem minus the FCI correlation energies for the subsystems $s$ and $t$. The reinterpretation of the higher order terms is equally simple.

In a computational scheme, we can either use the geminal correction terms directly as defined in Eq. (4), or approximate the terms in Eq. (5) by another size-extensive procedure, say a coupled cluster approach. A combination of different procedures is also possible, say a coupled cluster model for intrasystem correlation and an extended geminal model for intersystem correlation.

### 2.3 Decomposition of the intermolecular potential

Within this framework the intermolecular potential is defined as

$$U = E^{\mathrm{EXGF}} + \sum_{s=1}^{n} E^{s}_{\mathrm{nuc}} + \sum_{s<t} E^{s,t}_{\mathrm{nuc}} - \sum_{s=1}^{n} \left\{ E^{s}_{\mathrm{nuc}} + E^{\mathrm{EXGF},s}_{\mathrm{sep}} \right\} \tag{6}$$

In Eq. (6) $E^{\mathrm{EXGF}}$ is the energy of the supersystem based on the standard Hamiltonian, i.e. including one- and two-electron operators, $E^{s}_{\mathrm{nuc}}$ is the nuclear electrostatic energy for subsystem number $s$ (if there is only one nucleus in subsystem number $s$, $E^{s}_{\mathrm{nuc}} = 0$), $E^{s,t}_{\mathrm{nuc}}$ is the nuclear electrostatic energy between the subsystems number $s$ and $t$, and $E^{\mathrm{EXGF},s}_{\mathrm{sep}}$ is the energy for the isolated subsystem number $s$. By following the derivation in Ref. [18] we obtain

$$\begin{aligned} U &= \Delta_{\mathrm{dist}} + \Delta_{\mathrm{int}} \\ &= \sum_{s=1}^{n} \Delta^{s}_{\mathrm{dist}} + \sum_{s<t}^{n} \left\{ \Delta^{s,t}_{\mathrm{Coul}} + \Delta^{s,t}_{\mathrm{exch}} + \Delta^{s,t}_{\mathrm{corr}} \right\} \\ &\quad + \sum_{s<t<u}^{n} \Delta^{s,t,u}_{\mathrm{corr}} + \cdots \end{aligned} \tag{7}$$

The explicit form of the terms in Eq. (7) is given in Ref. [9], but the terms have simple interpretations. $\Delta^{s}_{\mathrm{dist}}$ denotes the distortion of subsystem number $s$, i.e. the change in energy of the subsystem in the presence of the other subsystems, $\Delta^{s,t}_{\mathrm{Coul}}$ denotes the Coulomb interaction between the distorted charge distributions of subsystems number $s$ and $t$, $\Delta^{s,t}_{\mathrm{exch}}$ and $\Delta^{s,t}_{\mathrm{corr}}$ are, respectively, the exchange and correlation terms related to these systems. In Eq. (7) there is a slight notational change:

$$\Delta^{s,t}_{\mathrm{corr}} = E^{s,t}_{\mathrm{corr}} \tag{8}$$

$$\Delta^{s,t,u}_{\mathrm{corr}} = E^{s,t,u}_{\mathrm{corr}} \tag{9}$$

The expressions for the intermolecular potential in Eq. (7) has the structure of a sum of one-body terms, two-body terms up to $n$-body terms. However, it should not be confused with the conventional way of writing the potential in terms of two-body potentials, three-body potentials up to $n$-body potentials. In Eq. (7), all terms are in a sense $n$-body terms since the perturbed state of a subsystem depends on all its partner subsystems.

The intermolecular potential can be expressed as a sum of effective intrasystem terms:

$$\begin{aligned} U &= \sum_{s=1}^{n} \Bigg\{ \Delta^{s}_{\mathrm{dist}} + \frac{1}{2} \sum_{\substack{t \\ t\neq s}}^{n} \Delta^{s,t}_{\mathrm{int}} \\ &\quad + \frac{1}{3} \left[ \sum_{s<t<u}^{n} \Delta^{s,t,u}_{\mathrm{int}} + \sum_{t<s<u}^{n} \Delta^{t,s,u}_{\mathrm{int}} + \sum_{t<u<s}^{n} \Delta^{t,u,s}_{\mathrm{int}} \right] + \cdots \Bigg\} \\ &= \sum_{s=1}^{n} \Delta^{s}_{\mathrm{eff,add}} \end{aligned} \tag{10}$$

For simplicity, we have introduced the subscript "int" on the interaction terms in Eq. (10). The definition of the corresponding terms should be obvious. The expression of the potential given by Eq. (10) is useful when an extended system is considered. If the system is periodic, we can restrict the calculation to the effective additive terms for the subsystems in the unit cell.

## 3 Numerical models

In dealing with a complex comprising a large number of subsystems, a straightforward or brute force application of a conventional ab initio quantum chemistry model is not feasible. Novel developments are highly requested. In this work, we shall introduce three new elements in a computational scheme for intermolecular interactions. First, intra- and intersystem contributions to the intermolecular potential shall be calculated by using model systems rather than the whole complex. Second, dual basis sets shall be adopted, i.e. a combination of small and large basis sets. Third, Cholesky decomposition of the two-electron integral matrix shall be used in order to reduce storage requirements and computation time.

### 3.1 Partner subsystems

The key idea is that for weakly interacting subsystems, the perturbed state of a subsystem in the complex is essentially determined by the subsystems in the vicinity of the system. To make use of this fact, we introduce for each subsystem a set of partner subsystems. If $R^{s,t}_{\text{min}}$ is the minimum distance between the nucleus of subsystem number $s$ and the nucleus of subsystem number $t$, then the partner subsystems for subsystem number $s$, $\Omega^{\text{partner}}_{s}$, includes all subsystem for which $R^{s,t}_{\text{min}} \leq R^{\text{threshold}}$, where $R^{\text{threshold}}$ is a chosen threshold distance. The model system for subsystem number $s$ consists then of subsystem number $s$ and its partner subsystems $\Omega^{\text{partner}}_{s}$. When we calculate the intrasystem energy for subsystem number $s$, we use the model system instead of the whole complex.

When we consider the interaction energy between two subsystems, say subsystems number $s$ and $t$, we introduce the partner subsystems for this pair of subsystems:

$$\Omega^{\text{partner}}_{s,t} = \Omega^{\text{partner}}_{s} \cup \Omega^{\text{partner}}_{t} - \Omega^{\text{partner}}_{s} \cap \Omega^{\text{partner}}_{t} \tag{11}$$

The model system for this pair of subsystems is then subsystems number $s$ and $t$ plus the partner subsystems $\Omega^{\text{partner}}_{s,t}$. The calculation of the intersystem energy for the pair $(s, t)$ is then performed with the model system as the physical system.

In principle, the three-body and higher-order interaction terms can be obtained by a similar procedure.

### 3.2 Dual basis sets

Dual basis sets have been used by King and coworkers [20, 21] in the calculation of self-consistent field (SCF) wave functions for Rydberg states, and Jurgens–Lutovski and Almlöf [22] introduced dual basis sets in the calculation of the second-order Møller–Plesset correlation energy. More recently, Wolinski and Pulay [23] have elaborated on the ideas of Jurgens–Lutovski and Almlöf. A dual basis approach has also been implemented in the program package MOLPRO [24]. The idea of Jurgens–Lutovski and Almlöf was to use a smaller basis set for the SCF wave function and a larger basis set for the correlation part. In order to satisfy the orthogonality condition between occupied orbitals (small basis) and virtual orbitals (large basis), the small basis was chosen as a subset of the large basis.

In this work, we use the dual basis concept in a slightly different manner. The small basis set is used for the partner subsets in a calculation. This implies that in the calculation of the intrasystem energy of subsystem number $s$, the large basis set is utilized for subsystem number $s$ and the small basis sets for the partner subsystems $\Omega^{\text{partner}}_{s}$. Similarly, for the calculation of the interaction energy between subsystems number $s$ and $t$, the large basis sets are utilized for the subsystems number $s$ and $t$, and the small basis sets are associated with the partner subsystems $\Omega^{\text{partner}}_{s,t}$. Since small and large basis sets are associated with different subsystems, there is no requirement that the small basis should be a subset of the larger one for a given subsystem.

### 3.3 Cholesky decomposition

The idea of a Cholesky decomposition of the two-electron integral matrix was first suggested by Beebe and Linderberg [25], and later Røeggen and coworkers [17,26] used this approach in a large number of studies of intermolecular interactions (see [17] for references to previous works). More recently Koch et al. [27] have devised an efficient algorithm for the decomposition.

Let the atomic orbital basis be denoted $\{\mathcal{X}_\mu;\ \mu = 1, \ldots, m\}$. A two-electron integral (in Mullikan's notation) $[\mu\nu \mid \lambda\sigma]$ is related to the integral tables (obtained by the Cholesky decomposition) $\{L_{\mu\nu;t},\ t = 1, \ldots, r_\delta\}$ by the relation

$$[\mu\nu \mid \lambda\sigma] = \sum_{t=1}^{r_\delta} L_{\mu\nu;t} L_{\lambda\sigma;t} \tag{12}$$

where $r_\delta$ is the effective numerical rank of the two-electron integral matrix. The theoretical maximum value of $r_\delta$ is $m(m+1)/2$. However, $r_\delta$ is in practice, considerably smaller. If we write $\delta = 10^{-p}$, then in most cases $r_\delta$ satisfies the inequality [26]

$$pm < r_\delta < (p+1)m \tag{13}$$

Compared with the storage of the two-electron integral matrix, the storage of the integral tables leads to a large reduction of storage requirements. The storage requirement can be further reduced by storing only the non-negligible elements of the integral tables [26,27].

A second advantage of using integral tables is the simplicity in obtaining transformed two-electron integrals. This transformation is performed according to the formulas

$$\psi_i = \sum_{\mu=1}^{m} \mathcal{X}_\mu U_{\mu i} \tag{14}$$

$$L_{ij;t} = \sum_{\mu,\nu=1}^{m} U_{\mu i} L_{\mu\nu;t} U_{\nu j} \tag{15}$$

$$[ij \mid kl] = \sum_{t=1}^{r_\delta} L_{ij;t} L_{kl;t} \tag{16}$$

It is obvious that an algorithm defined by Eqs. (14), (15) and (16) can be effectively coded for parallel processor computers.

### 3.4 Elimination of BSSE and localization of orbitals

The BSSE is eliminated by the Boys–Bernardi counterpoise correction scheme [28]. In the calculation of the intrasystem energy for the isolated system, one utilizes the full basis associated with a subsystem and its partner subsystems. For a given model system one calculates the occupied orbitals for *all* the isolated subsystems of this model system using the full model system basis. The orbitals for the isolated subsystems are utilized in two ways. First, they are used as start orbitals in the iterative procedure for determining the occupied orbitals of the model system. Second, they serve as target orbitals in the minimal distortion localization procedure [2,19]. The localized orbitals are obtained by minimizing the functional

$$\mathcal{L} = \sum_i w_i \parallel \varphi_i^{\text{modelsyst}} - \varphi_i^{\text{isolated}} \parallel^2 \tag{17}$$

In Eq. (17), $\{\varphi_i^{\text{modelsyst}}\}$ denote the localized orbitals to be determined while $\{\varphi_i^{\text{isolated}}\}$ are the corresponding orbitals of the isolated subsystems. The weight factors $\{w_i\}$ are included to give some preference to the innermost orbitals. Physically, we expect core orbitals to be less affected by the interaction with the neighbouring subsystems than valence orbitals. Hence, we choose (somewhat arbitrarily)

$$w_i = \left|\langle\varphi_i^{\text{isolated}} \mid F\,\varphi_i^{\text{isolated}}\rangle\right|^2 \tag{18}$$

where $F$ is the Fock operator. By this choice we obtain the smallest distortion of the core orbitals with respect to the orbitals of the isolated subsystems.

### 3.5 EXGF model based on an extended geminal model

In the first implementation of the advocated EXGF model, the electron correlation terms are calculated according to the extended geminal expansion, i.e. Eq. (4). Furthermore, the expansion is truncated at the double-pair level. Hence,

$$E^{\text{EXGF}} = E^{\text{RHF}} + \sum_{s=1}^{n}\left\{\sum_{K=1}^{N_s}\epsilon_{s,K} + \sum_{K_1<K_2}^{N_s}\epsilon_{s,K_1K_2}\right\} + \sum_{s<t}^{n}\sum_{K=1}^{N_s}\sum_{L=1}^{N_t}\epsilon_{s,K;t,L} \tag{19}$$

As for the details concerning the calculation of $\{\epsilon_K\}$ and $\{\epsilon_{KL}\}$, we refer to our previous works [2,18].

## 4 Test calculations on helium complexes

In this section, we shall present test calculations on different helium complexes: helium dimer; atoms in infinite, one-dimensional lattice; and infinite, two-dimensional, hexagonal latttice. We shall focus on the binding energy per atom. But we shall also look at the character of bonding and the difference in bonding when we consider the three types of clusters.

### 4.1 Computational details

For all calculations, we adopt family-type basis sets, i.e. if $\eta$ is the exponent of a Gaussian- type function (GTF) of angular momentum $\ell$, then the same exponent is included in the sets of exponents for all subsets of GTFs of lower angular momentum. Furthermore, the basis is an even-tempered one, i.e. the exponents form a geometrical series

$$\eta_i = \alpha\beta^{i-1}, \quad i = 1, 2, \ldots, m\,. \tag{20}$$

Integral calculations can be simplified by using family-type basis sets since fewer Hermite functions are required in the calculation of the two-electron matrix. This feature is implemented in our code for the decomposition of the two-electron integral matrix. The details of this approach will be discussed elsewhere. Unfortunately, there are very few optimized family-type basis sets to be found in the literature. Hence, we have to construct the basis sets.

The procedure for the construction of the large basis set is as follows. First, an uncontracted $(16s, 4p, 3d, 2f, 1g)$ set of GTFs is determined by energy minimization. The exponent of the $g$-type functions is number 5 in the ascending sequence of exponents. The optimized set yields an RHF energy for the ground state of the helium atom equal to $-2.86167435E_\text{h}$ ($-2.86168000E_\text{h}$ [29]) and a correlation energy equal to $-0.04148619E_\text{h}$ ($-0.04204529E_\text{h}$ [30]), the exact values in parentheses. Second, the optimized set is augmented with three sets of diffuse function in each symmetry, the exponents chosen as an even-tempered extension. Third, two sets of $h$-type functions with small exponents are added. Accordingly, the large basis comprises an uncontracted $(19s, 7p, 6d, 5f, 4g, 2h)$ set of GTFs. The exponents of the polarization functions and the exponents for the most diffuse $s$-type functions are given in Table 1.

The small basis is an uncontracted $(12s, 2p, 1d)$ set of GTFs. The exponent of the $d$-type function is number 3 in the ascending sequence of exponents. The exponents are obtained by energy minimization. The resulting even-tempered parameters are $\alpha = 0.2133784$ and $\beta = 3.2924$. The RHF and correlation energy are $-2.86146707E_\text{h}$ and $-0.03935317E_\text{h}$, respectively.

For the truncated virtual spaces, we use 82 natural orbitals for both the single- and double-pair correlation terms.

### 4.2 Helium dimer

The helium dimer is included in order to evaluate the quality of the calculation. The interatomic potential is calculated for the interatomic distances, 5.60, 5.61 and 5.62 a.u., close to the minimum. A parabolic fit yields a well depth of $34.60\mu E_\text{h}$ and an equilibrium distance of 5.6109 a.u. This result compares favourably with the exact quantum Monte Carlo calculation of Anderson [31]: a well depth of $(34.77 \pm 0.06)\mu E_\text{h}$ and equilibrium distance of 5.6 a.u.

A key feature in our approach is the approximation of the double-pair correlation terms. The term $\epsilon_{KL}$ is written as a full CI term plus a basis set extension (BSE) based on an

**Table 1** Orbital exponents of the most diffuse $s$-type functions and the polarization functions for the $(19s, 7p, 6d, 5f, 4g, 2h)$ GTF basis

| Exponent/symmetry | $s$ | $p$ | $d$ | $f$ | $g$ | $h$ |
|---|---|---|---|---|---|---|
| 17. 1240744 | x | | | | | |
| 6.5459000 | x | x | x | x | x | |
| 2.5022554 | x | x | x | x | x | |
| 0.9565196 | x | x | x | x | x | x |
| 0.3656421 | x | x | x | x | x | x |
| 0.1397714 | x | x | x | x | | |
| 0.0534294 | x | x | x | | | |
| 0.0204241 | x | x | | | | |
| 0.0078074 | x | | | | | |

MP2-type correction [17]:

$$\epsilon_{KL} = \epsilon_{KL}^{\mathrm{FCI}} + \epsilon_{KL}^{\mathrm{BSE}} \tag{21}$$

At the internuclear distance $R = 5.61$ a.u. we have $\epsilon_{KL}^{\mathrm{FCI}} = -66.47\mu E_\mathrm{h}$ and $\epsilon_{KL}^{\mathrm{BSE}} = -0.12\mu E_\mathrm{h}$. Hence, the four-electron FCI term accounts for 99.8% of the intersystem correlation energy obtainable with the adopted basis set.

The threshold used in the Cholesky decomposition of the two-electron integral matrix, affects the calculated potential. In Table 2 we display values of the interatomic potential for the equilibrium distance $R_\mathrm{eq} = 5.61$ a.u. based on different values of the threshold $\delta^{\mathrm{Chol}}$. We notice that for $\delta^{\mathrm{Chol}} < 10^{-6} E_\mathrm{h}$, the values of the potential differ with less than $10^{-9} E_\mathrm{h}$. The variation which is observed for the three values $10^{-6} E_\mathrm{h}$, $10^{-7} E_\mathrm{h}$ and $10^{-8} E_\mathrm{h}$ is likely to be due to numerical round-off errors. It is a bit remarkable that a threshold value as large as $10^{-4} E_\mathrm{h}$ yields only an error in the potential of the order of $0.01\mu E_\mathrm{h}$. The reason might be that the occupied orbitals are $s$-type orbitals which are very well described by the first (and dominant) tables in the decomposition. On the basis of the information in Table 2, it seems safe to conclude that a decomposition threshold less than $10^{-6} E_\mathrm{h}$ yields errors in the potentials which in magnitude are smaller than $10^{-2}\mu E_\mathrm{h}$.

Table 3 displays a decomposition of the interatomic potential for selected values of the interatomic distance; i.e. multiples of the equilibrium distance $R_\mathrm{eq} = 5.61$ a.u. The decomposition is of interest when we consider the one- and two-dimensional lattices in the next subsection. We notice in particular that when $R \geq 2R_\mathrm{eq}$, the interatomic potential is completely determined by the correlation component.

### 4.3 Basis sets and number of partner subsystems

The lattice constant is equal to the equilibrium distance for the dimer potential, i.e. 5.61 a.u. The decomposition threshold for the Cholesky procedure is $10^{-8} E_\mathrm{h}$.

**Table 2** Interatomic potential for the helium dimer as a function of the Cholesky two-electron integral threshold

| $\delta^{\mathrm{Chol}}$ ($E_h$) | $U$ ($R$=5.61 a.u.) ($\mu E_h$) | $E^{\mathrm{total}}(\delta^{\mathrm{Chol}}) - E^{\mathrm{total}}(\delta^{\mathrm{Chol}} = 10^{-8}$ a.u.) ($\mu E_h$) |
|---|---|---|
| $10^{-3}$ | −34.8772 | −1.9024 |
| $10^{-4}$ | −34.6130 | 0.0525 |
| $10^{-5}$ | −34.6056 | 0.0106 |
| $10^{-6}$ | −34.6017 | 0.0039 |
| $10^{-7}$ | −34.6022 | 0.0043 |
| $10^{-8}$ | −34.6018 | 0.0[a] |

[a] $E^{\mathrm{tot}}(\delta^{\mathrm{Chol}} = 10^{-8}\,\text{Å}) = -5.8066955997\,E_\mathrm{h}$

In the application of the procedure advocated in this work, two questions must be addressed first: the size of the basis sets for the partner subsystems, and the number of partner subsystems required for the model systems. As for the first question, we have considered four different basis sets. The smallest one is the $(12s, 2p, 1d)$ GTF set defined in Sect. 4.1. This set is augmented with one and two sets of diffuse functions in each symmetry, constructed as an even-tempered extension of the $(12s, 2p, 1d)$ set, yielding a $(13s, 3p, 2d)$ and a $(14s, 4p, 3d)$ set. The fourth set is an energy optimized $(14s, 3p, 2d, 1f)$ GTF set. Table 4 displays the effective one-body potential adopting these four different basis sets. The $(14s, 4p, 3d)$ yields the "best" result, but the variation is quite small. Since the result pertaining to the smallest set, deviates only $0.01\mu E_\mathrm{h}$ from the result of the $(14s, 4p, 3d)$ set, we consider the $(12s, 2p, 1d)$ set to be appropriate for the calculations on the one- and two-dimensional lattices.

The answer to the second question, i.e. the number of required partner subsystems, can be found in the results presented in Table 5. The binding energy per atom is practically stable when we increase the number of partner subsystems from two to four or six. Hence, for helium clusters with nearest neighbour (nn) distances equal to 5.61 a.u., it is sufficient to include only the nearest neighbour atoms in the set of partner atoms.

As for the character of the bonding in a one-dimensional lattice of atoms, we postpone our comments to the next subsection where we compare three different clusters: dimer, one- and two-dimensional lattices of atoms.

### 4.4 Hexagonal lattice of helium atoms

In this subsection, we consider a two-dimensional hexagonal lattice with lattice parameter equal to 5.61 a.u. Since we have calculated the interatomic interactions independently, i.e. in different runs on the computer, the Cholesky decomposition threshold varied between $1.0 \times 10^{-7} E_\mathrm{h}$ and $2.3 \times 10^{-7} E_\mathrm{h}$ due to a fixed number of integral tables which can be stored on each processor. As demonstrated in Table 2, this variation will hardly affect the results.

In Table 6, we present a decomposition of the interaction energy between atoms in this lattice. We notice that with distances larger than or equal to two times the lattice parameter (3nn), the interaction energy is completely determined by the interatomic correlation energy. Hence, the contribution to the binding energy per atom from pairs with large interatomic distances can be easily estimated. The interatomic distance for the (5nn)-pairs is three times the lattice constant and the corresponding interatomic correlation energy is

**Table 3** Decomposition of the interatomic potential for the helium dimer

| $R$ (a.u.) | $\Delta^{\mathrm{dist}}$ ($\mu E_h$) | $\Delta^{1,2}_{\mathrm{Coul}}$ ($\mu E_h$) | $\Delta^{1,2}_{\mathrm{exch}}$ ($\mu E_h$) | $\Delta^{1,2}_{\mathrm{corr}}$ ($\mu E_h$) | $\Delta^{1,2}_{\mathrm{int}}$ ($\mu E_h$) | $U$ ($\mu E_h$) |
|---|---|---|---|---|---|---|
| 5.61 | 50.31 | −44.32 | −24.24 | −66.66 | | −34.603 |
| 11.22 | 0.0 | 0.0 | 0.0 | −0.794 | −0.794 | −0.794 |
| 16.83 | 0.0 | 0.0 | 0.0 | −0.066 | −0.066 | −0.066 |
| 22.44 | 0.0 | 0.0 | 0.0 | −0.012 | −0.012 | −0.012 |

**Table 4** The effective one-body potential of a one-dimensional lattice of helium atoms for different basis set for the partner subsystems

| Basis:GTF | $\Delta^{s}_{\mathrm{eff,add}}(\mu E_h)$ |
|---|---|
| $12s, 2p, 1d$ | −35.49 |
| $13s, 3p, 2d$ | −35.47 |
| $14s, 4p, 3d$ | −35.50 |
| $14s, 3p, 2d, 1f$ | −35.48 |

The distance between nearest neighbour atoms: 5.61 a.u.; number of partner subsystems: two

**Table 5** Effective one-body potential of a one-dimensional lattice of helium atoms for different number of partner subsystems; the small basis, i.e. ($12s$, $2p$, $1d$), is adopted for partner subsystems

| $N_{\mathrm{partner}}$ | $\Delta^{s}_{\mathrm{eff,add}}\ (\mu E_h)$ |
|---|---|
| 2 | −35.486 |
| 4 | −35.485 |
| 6 | −35.486 |

$-0.0657\mu E_{\mathrm{h}}$. The long-range interaction energy is given by the well-known formula

$$\Delta^{1,2}_{\mathrm{int}} = -\frac{C_6}{R^6_{12}} - \frac{C_8}{R^8_{12}} - \cdots \tag{22}$$

Standard and Certain [32] give upper and lower bounds to the coefficients $C_6$ and $C_8$: $(1.44, 1.47)E_{\mathrm{h}}$ and $(13.9, 14.2)E_{\mathrm{h}}$, respectively. By including only the two dominant terms in Eq. (22) and using the average value of the upper and lower bounds of $C_8$, we obtain $C_6 = 1.443E_{\mathrm{h}}$ when $\Delta^{1,2}_{\mathrm{int}}$ is set equal to our calculated value of $-0.0657\mu E_{\mathrm{h}}$. In the estimate of the contribution to the binding energy per atom, from pairs of atoms with large interatomic distances, i.e. $R_{12} \geq 16.83$ a.u., the average values of the bounds to $C_6$ and $C_8$ are adopted.

The distortion energy of an atom in the hexagonal lattice, $\Delta_{\mathrm{dist}}$, is $293.34\mu E_{\mathrm{h}}$. Hence, we obtain a binding energy per atom equal to $114.79\mu E_{\mathrm{h}}$.

In Tables 7, 8 and 9 we perform comparisons among three different complexes: dimer, atoms in one- and two-dimensional lattices. First of all, we notice the strong accordance between dimer energy components and the corresponding components for atoms in the one-dimensional lattice. Neglecting the three-body correlation terms for the time being, we may state that the binding energy per atom for a one-dimensional lattice can be calculated by using only the dimer potentials. Second, not surprisingly, it is the nearest neighbour structure which is important for describing the deviation from

**Table 6** Decomposition of the interaction energy between pairs of atoms in a two-dimensional hexagonal lattice, and contribution from different pairs to the binding energy per atom (lattice constant: 5.61 a.u.)

| Pairs of atoms | Number of pairs in each group | $\Delta^{1,2}_{\mathrm{Coul}}(\mu E_h)$ | $\Delta^{1,2}_{\mathrm{exch}}(\mu E_h)$ | $\Delta^{1,2}_{\mathrm{corr}}(\mu E_h)$ | $\Delta^{1,2}_{\mathrm{int}}(\mu E_h)$ | $\frac{1}{2}\Sigma\Delta^{1,2}_{\mathrm{int}}\ (\mu E_h)$ |
|---|---|---|---|---|---|---|
| 1nn | 6 | −42.85 | −23.63 | −66.35 | −132.83 | −398.49 |
| 2nn | 6 | −0.01 | 0.0 | −1.92 | −1.93 | −5.79 |
| 3nn | 6 | 0.0 | 0.0 | −0.80 | −0.80 | −2.40 |
| 4nn | 12 | 0.0 | 0.0 | −0.14 | −0.14 | −0.84 |
| 5nn | 6 | 0.0 | 0.0 | −0.07 | −0.07 | −0.21 |
| $R_{12} > 16.83$ a.u. | $\infty$ | | | | | −0.40[a] |

nn: Nearest neighbour

[a] Estimated

**Table 7** Decomposition of the interaction energy for pairs of nearest neighbour atoms in different complexes

| Complex | $\Delta^{1,2}_{\mathrm{Coul}}\ (\mu E_h)$ | $\Delta^{1,2}_{\mathrm{exch}}\ (\mu E_h)$ | $\Delta^{1,2}_{\mathrm{corr}}(\mu E_h)$ | $\Delta^{1,2}_{\mathrm{int}}(\mu E_h)$ |
|---|---|---|---|---|
| Dimer[a] | −44.32 | −24.24 | −66.66 | −135.22 |
| One-dimensional lattice[a] | −44.34 | −24.25 | −66.65 | −135.24 |
| Two-dimensional lattice[a] | −42.85 | −23.63 | −66.35 | −132.83 |

[a] Distance between nearest neighbour atoms: 5.61 a.u.

**Table 8** Decomposition of the interaction energy for pairs of atoms at a distance $R = 11.22$ a.u. ($2\times$ nearest neighbour distance), in different complexes

| Complex | $\Delta^{1,2}_{\mathrm{Coul}}\ (\mu E_h)$ | $\Delta^{1,2}_{\mathrm{exch}}\ (\mu E_h)$ | $\Delta^{1,2}_{\mathrm{corr}}\ (\mu E_h)$ | $\Delta^{1,2}_{\mathrm{int}}\ (\mu E_h)$ |
|---|---|---|---|---|
| Dimer | 0.0 | 0.0 | −0.794 | −0.794 |
| One-dimensional lattice | 0.0 | 0.0 | −0.797 | −0.797 |
| Two-dimensional lattice | 0.0 | 0.0 | −0.794 | −0.794 |

**Table 9** Contribution to the binding energy per atom per number of nearest atoms, in different complexes including only the nearest neighbours

| Complex | $\Delta^{\mathrm{dist}}/N_{\mathrm{nn}}\ \ (\mu E_h)$ | $\Delta^{1,2}_{\mathrm{int}}/2\ \ (\mu E_h)$ | $\Delta^{\mathrm{dist}}/N_{\mathrm{nn}} + \Delta^{1,2}_{\mathrm{int}}/2\ (\mu E_h)$ |
|---|---|---|---|
| Dimer[a] | 50.31 | −67.61 | −17.30 |
| One-dimensional lattice[a] | 50.32 | −67.62 | −17.30 |
| Two-dimensional lattice[a] | 48.89 | −66.42 | −17.53 |

[a] Distance between nearest neighbour atoms: 5.61 a.u.

a pure pair potential approach. Interaction energies between non-nearest neighbour atoms are practically the same in the two lattices. Third, the contribution to the binding energy per atom per number of nearest neighbour atoms differs by only $0.23\mu E_\mathrm{h}$ for the two lattices, i.e. only 1.3% of the binding energy in question. One might perhaps be tempted to suggest that for helium clusters the genuine $N$-body terms ($N > 2$) are not very important. However, a word of caution is appropriate. When we consider the distortion energy and the interaction energy separately Table 9 we notice larger differences between corresponding components for the two lattices. The partitioned distortion energies and the partitioned interaction energies differ in magnitude by $1.43\mu E_\mathrm{h}$ and $1.20\mu E_\mathrm{h}$, respectively. However, the differences have opposite sign. Hence, a large cancellation occurs in the calculation of the binding energy. Such a large cancellation compared with the pair potential approximation, might not be the case when other types of structures are considered. In a preliminary calculation on atoms in a three-dimensional face-centred cubic lattice, using the advocated approach, the distortion energy per atom divided by the number of nearest neighbour atoms is $47.48\mu E_\mathrm{h}$ while the partitioned interaction energy between the nearest neighbour atoms is $-66.29\mu E_\mathrm{h}$. Accordingly, the binding energy in question is $18.81\mu E_\mathrm{h}$. For this particular structure, the genuine $N$-body terms represent 8.7%.

In this work, we have omitted three-body correlation terms. But they are not completely negligible. Røeggen and Almlöf [33] have calculated the three-body potential for the helium trimer for selected geometries. They demonstrated that when all three interatomic distances were larger than 5.5 a.u., then the three-body correlation term was well represented by the Axilrod–Teller triple dipole interaction [34], i.e.

$$\epsilon_{123}^{\mathrm{AT}} = C_9 \, \frac{(1 + 3\cos\gamma_1 \cos\gamma_2 \cos\gamma_3)}{R_{12}^3 R_{13}^3 R_{23}^3} \tag{23}$$

where $R_{12}$, $R_{13}$ and $R_{23}$ are the distances between the three atoms involved, and $\gamma_1$ is the angle defined by the sides $R_{12}$ and $R_{13}$ of the $\mathrm{He}_3$ triangle, and with similar definitions for $\gamma_2$ and $\gamma_3$. According to Standard and Certain [32], the average value of the upper and lower bounds to $C_9$ is $1.473E_\mathrm{h}$. On the basis of the Axilrod–Teller approximation, we arrive at the value of $0.66\mu E_\mathrm{h}$ for the three-body correlation contribution to the binding energy per atom, i.e. a relative contribution of 0.6%.

## 5 Concluding remarks

The advocated model satisfies the requirements formulated in the Sect. 1: the inherent conceptual structure facilitates interpretation, the model can be applied for any intersystem distance, it is size-extensive, basis set artefacts can be avoided, and finally, the model is feasible from a computational point of view. Test calculation on various helium systems indicate that the model is capable of producing very accurate PES. Work is now under way to consider helium atoms in infinite, three-dimensional lattices.

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## References

1. Chałasiński G, Szczęśniak MM (2000) Chem Rev 100:4227
2. Røeggen I (2005) Int J Quantum Chem 101:201
3. Maitland GC, Rigby M, Smith EB, Wakeham WA (1981) Intermolecular forces. Oxford University Press, Oxford
4. Hobza P, Zahradnik R (1988) Intermolecular complexes. The role of van der Waals systems, in physical chemistry and in biodisciplines. Elsevier, Amsterdam
5. Stone AJ (2002) The theory of intermolecular forces. Oxford University Press, Oxford
6. Nesbet RK (1969) Adv Chem Phys 14:1
7. Røeggen I (1983) J Chem Phys 79:5220
8. Stoll H (1992) Phys Rev B46:6700
9. Doll K, Dolg M, Fulde P, Stoll H (1995) Phys Rev B 52:4842
10. Doll K, Pykkyö P, Stoll H (1998) J Chem Phys 109:2339
11. Stoll H (1992) Chem Phys Lett 181:548
12. Paulus B, Fulde P, Stoll H (1996) Phys Rev B 54:2556
13. Rosciszewski K, Paulus B, Fulde P, Stoll H (1999) Phys Rev B 60:7905
14. Yu M, Kalvoda S, Dolg M (1997) Chem Phys 224:121
15. Stoll H (1992) J Chem Phys 97:8449
16. Paulus B (2004) Int J Quantum Chem 100:1026
17. Røeggen I (1999) Correlation and localization. In: Surján PR (ed) Topics in current chemistry, vol 203. Springer, Berlin Heidelberg Newyork
18. Røeggen I, Ahmadi GR, Wind PA (1993) J Chem Phys 99:277
19. Ahmadi G R, Røeggen I (1997) Theor Chem Acc 97:41
20. Havriliak S, King HF (1983) J Am Chem Soc 105:4
21. Havriliak S, Furlani TR, King HF (1984) Can J Phys 62:1336
22. Jurgens–Lutovski R, Almlöf J (1991) Chem Phys Lett 178:451
23. Wolinski K, Pulay P (2003) J Chem Phys 118:9497
24. MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions from J. Almlöf, R.D. Amos, A. Bernhardsson et al.
25. Beebe NHF, Linderberg J (1977) Int J Quantum Chem 12:683
26. Røeggen I, Wislöff–Nilssen E (1986) Chem Phys Lett 132:154
27. Koch H, Sánchez de Merás A, Pedersen TB (2003) J Chem Phys 118:9481
28. Boys SF, Bernardi F (1970) Mol Phys 19:553
29. Szalewicz K, Monkhorst HJ (1981) J Chem Phys 75:5785
30. Peckeris CL (1959) Phys Rev 115:1216
31. Anderson JB (2001) J Chem Phys 115:4546
32. Standard JM, Certain PR (1985) J Chem Phys 83:3002
33. Røeggen I, Almlöf J (1996) J Mol Struct (Theochem) 388:331
34. Axilrod BM, Teller E (1943) J Chem Phys 11:299