

Dispersion interactions within the Piris natural orbital functional theory: The helium dimer

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The authors have investigated the description of the dispersion interaction within the Piris natural orbital functional (PNOF) theory. The PNOF arises from an explicit antisymmetric approach for the two-particle cumulant in terms of two symmetric matrices, $\mathbf{\Delta}$ and $\mathbf{\Lambda}$. The functional forms of these matrices are obtained from the generalization of the two-particle system expressions, except for the off-diagonal elements of $\mathbf{\Delta}$. The mean value theorem and the partial sum rule obtained for the off-diagonal elements of $\mathbf{\Delta}$ provide a prescription for deriving practical functionals. In particular, the previous employed approximation $\{J_{pp}/2\}$ for the mean values $\{J_p^*\}$ affords several molecular properties but it is incapable to account for dispersion effects. In this work, the authors analyze a new approach for J_p^* obtained by factorization of the matrix $\mathbf{\Delta}$ within the bounds on its off-diagonal elements imposed by the positivity conditions of the two-particle reduced density matrix. Additional terms for the matrix elements of $\mathbf{\Lambda}$ proportional to the square root of the holes are again introduced to describe properly the occupation numbers of the lowest occupied levels. The authors have found that the cross products between weakly occupied orbitals must be removed from the functional form of $\mathbf{\Lambda}$ to obtain a correct long-range asymptotic behavior. The PNOF is used to predict the binding energy as well as the equilibrium distance of the helium dimer. The results are compared with the full configuration-interaction calculations and the corresponding experimental data. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743019]

I. INTRODUCTION

The dispersion or van der Waals (vdW) interactions play a fundamental role in the stability and conformation of biomolecular and condensed-phase systems. They constitute the weakest of the intermolecular forces and are typically a component in the force balance which dictates the resulting behavior. Even when short-range forces are dominant, an accurate estimate of these long-range forces is necessary for a correct evaluation of experimental results.

The description of vdW complexes is a difficult task since they arise mainly from electron correlation. The conventional density functional theory (DFT) fails when it is used to describe the weak long-range vdW interaction.¹ This issue continues being a major challenge for DFT approximations² despite the recent progress in practical DFT calculations to account for the dispersion interactions.^{3,4} Highly correlated *ab initio* methods capable of describing dispersion properly can instead be employed, but these methods are computationally much more demanding than DFT.

An alternative formalism to DFT is the natural orbital functional theory⁵⁻¹⁵ (NOFT), which provides an exact description of Coulombic systems in terms of the natural orbitals (NOs) and their occupation numbers (ONs). The theoretical investigation in quantum chemistry of NOFT has increased quickly in the last several years¹⁶⁻³⁸ (for a recent review on NOFT, see Ref. 39). A general description of weakly interacting systems within density matrix functional theory was presented by Cioslowski and Pernal.⁴⁰ From the asymptotic behavior of the total energy of a system consist-

ing of two weakly interacting subsystems, and upon the assumption of a complete localization of the spin orbitals within the subsystems, they obtained certain conditions on the exchange-correlation energy as a functional of the one-particle reduced density matrix (1-RDM). Gritsenko and Baerends⁴¹ have recently obtained the potential-energy curve around the vdW minimum of the $^3\Sigma_u^+$ state of H_2 from an analysis of its configuration-interaction wave function and the exact NOF of this two-electron triplet wave function employing only eight NOs.

Our aim in the present paper is to test the performance of the recently proposed NOF termed Piris natural orbital functional^{35,39} (PNOF) in the treatment of vdW interactions. Validation tests of this NOF for predicting several molecular properties have been performed³⁶ as well as an open-shell formulation.³⁷ The PNOF uses an explicit form for the cumulant^{42,43} of the two-particle reduced density matrix (2-RDM) in terms of two symmetric matrices $\mathbf{\Delta}$ and $\mathbf{\Lambda}$. These matrices are only functions of the ONs therefore, considering real orbitals, the PNOF depends solely on the Coulomb and exchange integrals. This functional reduces to the exact expression for the total energy in two-electron systems²⁰ and can be generalized to the N -electron systems with a suitable extension of $\mathbf{\Delta}$ and $\mathbf{\Lambda}$ matrices. The mean value theorem and the partial sum rule for matrix $\mathbf{\Delta}$ provide a prescription for deriving practical NOFs. Accordingly, practical implementations of PNOF can be improved by providing better approximations for the mean value J_p^* of the Coulomb interactions.

The He_2 is a paradigmatic molecule for the theory of

vdW interaction so we will focus our discussion on the helium dimer. A large number of papers have been devoted to the computation of the dispersion interaction on the helium dimer using DFT and *ab initio* methods.^{44,45} Results from these calculations with high level of accuracy are listed in Ref. 46. In our previous works,^{35,36} we have used the approximation $J_p^* \approx J_{pp}/2$. Unfortunately, the potential obtained using this approximation is repulsive for all interatomic distances of He₂. In the present work, we analyze alternatively a new approach for J_p^* achieved by factorization of the matrix Δ . The new ansatz is obtained from the partial sum rule for matrix Δ which fulfils the constraints imposed by the well-known positivity conditions of the 2-RDM. This leads to an accurate interaction potential between He atoms.

We start with a presentation of the basic concepts relevant to PNOF theory (Sec. II). Our new ansatz for the matrix Δ and the corresponding approximation for J_p^* are discussed in detail here. We end with a presentation of the results obtained for the helium dimer (Sec. III).

II. THEORY

We briefly describe here the theoretical framework of our approach. A detailed description of the PNOF can be found in Ref. 39.

In this paper, are concerned only with closed-shell systems. In this case of spin compensated systems, the PNOF for N -electron systems is

$$E = 2 \sum_p n_p h_{pp} + 2 \sum_{pq} (n_q n_p - \Delta_{qp}) J_{pq} - \sum_{pq} \Lambda_{qp} K_{pq}. \quad (1)$$

The orbitals $\{\varphi_p(\mathbf{r})\}$ constitute a complete orthonormal set of single-particle real wave functions, where p denotes the orbital and $\{n_p\}$ are their occupations. h_{pp} is the matrix element of the kinetic energy and nuclear attraction terms. $J_{pq} = \langle pq | pq \rangle$ and $K_{pq} = \langle pq | qp \rangle$ are the electron repulsion integrals. Note that if $\Delta_{qp} = 0$ and $\Lambda_{qp} = n_q n_p$, then our reconstruction functional yields the Hartree-Fock case. From the requirement that for any two-electron system ($N=2$) expression [Eq. (1)] should yield the *exact* energy functional of Ref. 20, one easily deduces that $\Delta_{qp} = n_q n_p$ and

$$\Lambda_{11} = -n_1 \quad \text{if } q = p = 1, \quad (2)$$

$$\Lambda_{qp} = [1 - 2\theta(0.5 - n_q)\theta(0.5 - n_p)]\sqrt{n_q n_p} \quad \text{if } q \neq p, \quad (3)$$

where $\theta(x)$ is the unit step function also known as the Heaviside function. The functional form [Eqs. (2) and (3)] of matrix Λ is readily generalized to

$$\Lambda_{pp} = -n_p \quad \text{if } q = p, \quad (4)$$

$$\Lambda_{qp} = [1 - 2\theta(0.5 - n_q)\theta(0.5 - n_p)]\sqrt{n_q n_p} \quad \text{if } q \neq p. \quad (5)$$

Equation (4) leads to diagonal elements of Δ equal to the square of the occupation numbers,

$$\Delta_{pp} = n_p^2, \quad (6)$$

and the sum rule that must fulfill the cumulant of the 2-RDM implies likewise the following constraint for nondiagonal elements of matrix Δ .³⁵

$$\sum'_q \Delta_{qp} = n_p h_p. \quad (7)$$

The primes indicates here that the $q=p$ term is omitted, and h_p denotes the hole $1-n_p$ in the NO p . Unfortunately, $\Delta_{qp} = n_q n_p$ violates the sum rule [Eq. (7)] in the general case of $N > 2$, therefore the functional form of the off-diagonal elements of Δ is unknown for N -electron systems. Nevertheless, the N -representability positivity necessary conditions of the 2-RDM impose several bounds on these quantities,³⁵

$$\Delta_{qp} \leq n_q n_p, \quad \Delta_{qp} \leq h_q h_p, \quad q \neq p. \quad (8)$$

By taking into account Eq. (6), the energy functional [Eq.(1)] can be rewritten as

$$E = 2 \sum_p n_p h_{pp} + 2 \sum'_{pq} (n_q n_p - \Delta_{qp}) J_{pq} - \sum_{pq} \Lambda_{qp} K_{pq}. \quad (9)$$

It is not evident how to approach Δ_{qp} , for $q \neq p$, in terms of the ONs. Due to this fact, the energy term in Eq. (9) which involves Δ_{qp} is rewritten as

$$\sum'_{pq} \Delta_{qp} J_{pq} = \sum_p J_p^* \sum'_q \Delta_{qp} = \sum_p n_p h_p J_p^*, \quad (10)$$

where J_p^* denotes the mean value of the Coulomb interactions J_{pq} for a given orbital p taking over all orbitals $q \neq p$. Here, the sum rule for off-diagonal elements of matrix Δ [Eq. (7)] was used. Inserting this expression into Eq. (9), one obtains

$$E = \sum_p (2n_p h_{pp} + n_p^2 J_{pp}) + \sum'_{pq} (2n_q n_p J_{pq} - \Lambda_{qp} K_{pq}) + \sum_p n_p h_p (J_{pp} - 2J_p^*). \quad (11)$$

We have previously used the approximation $J_p^* \approx J_{pp}/2$ that eliminates the last term in Eq. (11). Hereafter, we refer to this approach as PNOF-1. The comparison with other theoretical methods showed that PNOF-1 predicts several molecular properties close to accurate *ab initio* methods such as CCSD(T), and in good agreement with the available experimental data.³⁶ Unfortunately, it does not bind the helium dimer so a new ansatz is needed in order to describe vdW interactions.

It is easy to verify that the consequence of D condition on matrix Δ ($\Delta_{qp} \leq n_q n_p$) is more restrictive than the consequence of Q condition ($\Delta_{qp} \leq h_q h_p$) between orbitals with ONs close to zero, whereas for Δ elements between orbitals with ONs close to one, the Q condition is predominant. Accordingly, let us decompose the off-diagonal elements of Δ as follows:

$$\begin{aligned} \Delta_{qp} &= h_q h_p \theta(n_q - 0.5) \\ &\quad \times \theta(n_p - 0.5) + n_q n_p \theta(0.5 - n_q) \theta(0.5 - n_p) \\ &\quad + f_{qp} [\theta(n_q - 0.5) \theta(0.5 - n_p) \\ &\quad + \theta(0.5 - n_q) \theta(n_p - 0.5)], \end{aligned} \quad (12)$$

which guarantees from the outset the constraints imposed by the positivity conditions of the 2-RDM for the off-diagonal elements of Δ between weakly and strongly occupied orbit-

als, respectively. The magnitudes $\{f_p\}$ are determined using Eq. (7), namely,

$$h_p \sum_{q=1}^F h_q + f_p \sum_{q=F+1}^{\infty} f_q = n_p h_p \quad \text{if } p \leq F, \quad (13)$$

$$f_p \sum_{q=1}^F f_q + n_p \sum_{q=F+1}^{\infty} n_q = n_p h_p \quad \text{if } p > F, \quad (14)$$

where F denotes the Fermi level. The trace of the 1-RDM equals the number of electrons,

$$\text{Tr } {}^1D = 2 \sum_{q=1}^{\infty} n_q = N, \quad (15)$$

and from Eq. (15), it follows readily that

$$\sum_{q=1}^F h_q = \sum_{q=F+1}^{\infty} n_q = S. \quad (16)$$

Combining this expression with Eqs. (13) and (14), one obtains

$$f_p = \frac{(1-S)}{\sum_{q=F+1}^{\infty} f_q} h_p \quad \text{if } p \leq F, \quad (17)$$

$$f_p = \frac{(1-S)}{\sum_{q=1}^F f_q} n_p \quad \text{if } p > F. \quad (18)$$

Considering the sum of over all f_p up to F on the left-hand side of the Eq. (17), or the sum of over all f_p from $F+1$ up to ∞ on the left-hand side of the Eq. (18), one finds the following result:

$$\sum_{p=1}^F f_p \sum_{q=F+1}^{\infty} f_q = S(1-S). \quad (19)$$

It is straightforward to verify that the off-diagonal elements of $\Delta_{qp} = f_q f_p$ satisfy the N -representability conditions [Eq. (8)] too. Taking into account the new approach for the off-diagonal elements of Δ [Eq. (12)] and Eqs. (17)–(19), the energy expression [Eq. (9)] becomes

$$\begin{aligned} E = & 2 \sum_{p=1}^{\infty} n_p h_{pp} - \sum_{p,q=1}^{\infty} \Lambda_{qp} K_{pq} + 2 \sum_{p,q=1}^{\infty} n_q n_p J_{pq} \\ & - 2 \sum_{p,q=1}^F h_q h_p J_{pq} - 2 \sum_{p,q=F+1}^{\infty} n_q n_p J_{pq} \\ & - 2 \frac{1-S}{S} \left(\sum_{q=1}^F \sum_{p=F+1}^{\infty} h_q n_p J_{pq} + \sum_{q=F+1}^{\infty} \sum_{p=1}^F n_q h_p J_{pq} \right). \end{aligned} \quad (20)$$

According to Eq. (10), the mean value J_p^* of the Coulomb interactions for a given orbital p taking over all orbitals $q \neq p$ is defined as

$$J_p^* = \frac{1}{n_p h_p} \sum_q n_q J_{pq}. \quad (21)$$

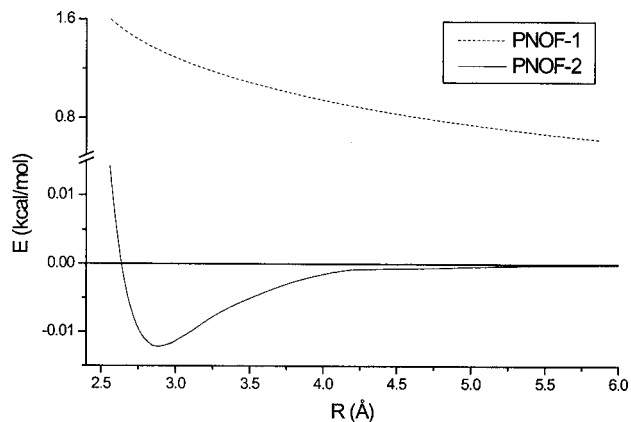


FIG. 1. Comparison of the He–He binding energy curves obtained by PNOF method with the aug-cc-pVTZ basis set.

It follows without difficulty that J_p^* is currently approximated by the following expressions:

$$J_p^* = \frac{1}{n_p} \left(\sum_{q=1}^F h_q J_{pq} + \frac{1-S}{S} \sum_{q=F+1}^{\infty} n_q J_{pq} \right) \quad \text{if } p \leq F, \quad (22)$$

$$J_p^* = \frac{1}{h_p} \left(\frac{1-S}{S} \sum_{q=1}^F h_q J_{pq} + \sum_{q=F+1}^{\infty} n_q J_{pq} \right) \quad \text{if } p > F. \quad (23)$$

In the case of N -electron systems, it was pointed out in Ref. 35 that the simple functional form [Eq. (5)] for the matrix elements of Λ between orbitals with ONs larger than 0.5 gives a wrong description for the lowest occupied levels. The ONs for these levels are identically equal to one. In order to ensure that these occupation numbers only are close to unity, an additional term proportional to the square root of the holes was introduced in the functional form of Λ_{qp} , namely,

$$\Lambda_{qp}^1 = \theta(n_q - 0.5) \theta(n_p - 0.5) \sqrt{h_q h_p} \quad \text{if } q \neq p. \quad (24)$$

In this study, we introduce two new additional terms proportional to the square root of the products of $h_q n_p$ and $n_q h_p$, respectively, in particular,

$$\begin{aligned} \Lambda_{qp}^2 = & - [\theta(n_q - 0.5) \theta(0.5 - n_p) \sqrt{h_q n_p} \\ & + \theta(0.5 - n_q) \theta(n_p - 0.5) \sqrt{n_q h_p}] \quad \text{if } q \neq p. \end{aligned} \quad (25)$$

To describe properly the energy values as a function of distance R between He atoms, we have found that the cross products between weakly occupied orbitals must be removed from the functional form of Λ . On the contrary case, the obtained functional overestimates the He₂ well depth. Accordingly, we will use the following expression for Λ :

$$\begin{aligned} \Lambda_{qp} = & \theta(n_q - 0.5) \theta(n_p - 0.5) (\sqrt{n_q n_p} + \sqrt{h_q h_p}) \\ & + \theta(n_q - 0.5) \theta(0.5 - n_p) (\sqrt{n_q n_p} - \sqrt{h_q n_p}) \\ & + \theta(0.5 - n_q) \theta(n_p - 0.5) (\sqrt{n_q n_p} - \sqrt{n_q h_p}). \end{aligned} \quad (26)$$

Henceforth, in this article, the new ansatz, Eq. (20) using the functional form of Λ [Eq. (26)], will be termed PNOF-2.

TABLE I. Comparison of the calculated and experimental values for the equilibrium (minimum energy) distance R_e (Å), dissociation energy D_e (kcal/mol), and vibrational wave number ω_e (cm^{-1}). Experimental values for R_e , D_e , and ω_e were taken from Ref. 47.

	R_e	D_e	ω_e
PNOF-2	2.889	0.012	33.2
FCI	3.009	0.020	31.2
Expt.	2.977	0.021	32.7

III. RESULTS

It is very difficult to obtain a reliable He–He interaction potential because He atoms bind very weakly with each other, being the experimental binding energy of only 0.021 kcal/mol at an equilibrium distance of 2.977 Å.⁴⁷ For long-range interactions, a diffuse basis set is needed for describing delocalized electrons. We have adopted the augmented correlation-consistent triple zeta (aug-cc-pVTZ) basis sets for He.⁴⁸ In fact, the most accurate available interaction potentials for the helium dimer have been calculated using large d-aug-cc-pV5Z and -6Z basis sets.^{49,50} Unfortunately, these sets are too large for our present implementation.

In Fig. 1, the PNOF potential-energy curves for the ground state of the He₂ molecule are displayed in the region $R=2.4\text{--}6.0$ Å. The calculated total energies of the helium dimer at various distances are referred to the dissociation limit for each approach in order to obtain the vdW interaction energies.

The PNOF-1 total energies are referred to the dissociation limit of $-5.791\,789\,47$ hartree for two He atoms. One can see from Fig. 1 that the PNOF-1 curve is purely repulsive, approaching the dissociation limit from above, which reflects that the mean value J_p^* is insufficient for the molecular binding in the He₂ molecule.

Figure 1 shows the PNOF-2 potential-energy curve for the ground state of the helium dimer around the vdW minimum. The PNOF-2 recovers enough correlation through the $\Delta-J$ term to produce a binding curve. The equilibrium bond distance and binding energy obtained using PNOF-2 are 2.889 Å and 0.012 kcal/mol, respectively. The calculated

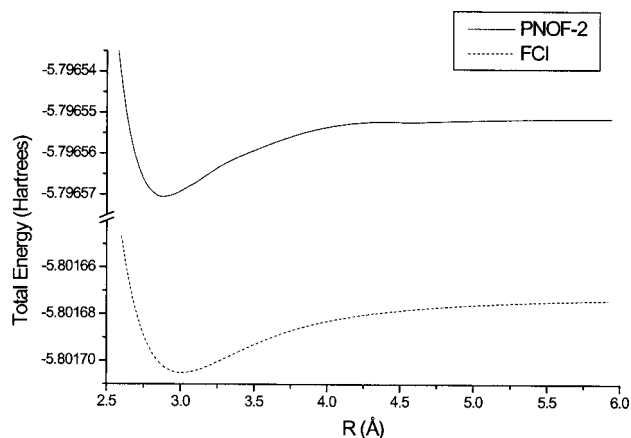


FIG. 2. Total energy values as a function of distance R between He atoms obtained by PNOF-2 and FCI methods with the aug-cc-pVTZ basis set.

TABLE II. Comparison of the He₂ dissociation energies D_e (kcal/mol) obtained at the PNOF-2 level of theory with different basis sets.

Basis set	D_e
cc-pVDZ	0.005
cc-pVTZ	0.007
aug-cc-pVTZ	0.012

PNOF-2 dissociation limit energy for two He atoms is of $-5.796\,551\,14$ hartree here. For the considered basis set, the latter energy is larger than the exact PNOF value of two helium atoms about 3 kcal/mol.

Table I compares the calculated and experimental equilibrium distance (R_e), well depth (D_e), and frequency (ω_e) for the helium dimer. The PNOF-2 error with respect to the experiment for R_e , D_e , and ω_e is 0.088 Å, 0.009 kcal/mol, and 0.5 cm^{-1} , respectively. In general, the results are in line with their corresponding experimental values, and represent an encouraging preliminary step, given the relative small basis sets (aug-cc-pVTZ) used for these calculations.

For comparison, we have included calculations based on full configuration-interaction (FCI) wave function carried out with the GAMESS package.⁵¹ With the aug-cc-pVTZ basis set, we have obtained FCI well depth of 0.020 kcal/mol, at an equilibrium distance of 3.009 Å. The PNOF-2 error with respect to the FCI for R_e , D_e , and ω_e is 0.12 Å, 0.008 kcal/mol, and 2.0 cm^{-1} , respectively. The calculated FCI dissociation limit energy for two He atoms is of $-5.801\,672\,79$ hartree here. We must note that at all distances R considered the calculated PNOF-2 total energies are larger than the FCI values (Fig. 2).

Clearly, for a proper description of the interaction energy of vdW complexes, the basis set superposition error (BSSE) should be considered. We have estimated the BSSE at the equilibrium distance using the counterpoise method.⁵² The counterpoise correction for the aug-cc-pVTZ basis set at the full CI level is 0.003 kcal/mol, one order of magnitude smaller than the dissociation energy. Table II compares the calculated dissociation energies at the PNOF-2 level of theory using different basis sets. Inspection of this table reveals that PNOF-2 yields D_e values closer to the experimental data as the basis set improves. Therefore, the results showed in Table I are mainly dominated by the dispersion interactions instead of being an spurious attractive contributions from the BSSE.

IV. CONCLUSIONS

We have carried out an analysis on the helium dimer of two approximate formulations of the PNOF. The potential-energy curve obtained using PNOF-1 is repulsive, approaching the dissociation limit from above. On the other hand, a reasonable account of the binding dispersion effects of the helium dimer has been achieved with the PNOF-2 approximation. Preliminary calculations with the latter approximate natural orbital functional yield the equilibrium distance, the binding energy, and the harmonic frequency in line with their corresponding experimental values, in spite of the relative small basis sets (aug-cc-pVTZ) used for these calculations. It

is therefore expected that larger basis set will lead to tighter match with respect to the experimental marks.

Finally, it is hoped that the PNOF-2 will constitute a first step towards an accurate treatment of the vdW interactions within the natural orbital functional theory.

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