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Fourth-Order Diagrammatic MB-RSPT Calculations of the Interaction Energy Between Two Helium Atoms

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The efficiency of the MB-RSPT in the calculations of the correlation contributions to the interaction energies was investigated, using He_2 as a model Van der Waals system. The attention has been focused on the convergency of the perturbation expansion in the calculations of the interaction energy and on the analysis of the fourth-order terms of MB-RSPT. The rôle of the renormalization term in the correct long-range behaviour of the interaction potential has been emphasized.

Key words: MB-RSPT calculations – He_2, interaction energy of ∼.

1. Introduction

The interaction energy between two ground state helium atoms has been investigated by *ab initio* calculations in numerous papers using both different basis sets and methods at different levels of accuracy. The very recent one, published by Silver [1], is the most closely related to the present work. Silver used the supermolecule approach, in which the interaction energy at a given internuclear distance r was defined as follows:

$$\Delta E(r) = E(\mathrm{He}_2, r) - 2E(\mathrm{He}) \qquad (1)$$

where $E(\mathrm{He}_2, r)$ was the calculated energy of the He_2 system at r and $E(\mathrm{He})$ was the calculated energy of an isolated atom. The energies $E(\mathrm{He}_2, r)$ and $E(\mathrm{He})$ were

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calculated [1] as a sum of the SCF contribution and correlation energies obtained from the second and third order Many-Body Perturbation Theory, using both "model" reference Hamiltonian, that is the Møller–Plesset [2] partitioning of the Hamiltonian and "shifted" reference Hamiltonian [3], equivalent to the Epstein–Nesbet partitioning [4]. Only the former one achieves a proper distance dependence at large r for the He_2 potential curve (see also the careful analysis of both partitionings by Malrieu and Spiegelmann [5]). In our work we have used the Many-Body Rayleigh–Schrödinger Perturbation Theory (MB-RSPT) exclusively with the Møller–Plesset partitioning. We proceeded with the perturbation expansion up to the sixth order for double excitations, using the iterative procedure [6, 7], and investigated also quadruple excitations at the fourth order [8–13]. We believe that this approach enables deeper insight, complementary to that obtained by Silver, into the efficiency of MB-RSPT, using He_2 as a model van der Waals system. Specifically, our attention has been focused to three main items:

(i) Convergency of the perturbation expansion in the calculations of the interaction energy.
(ii) Comparison of the simple dispersion energy with the second order "supermolecule" interaction energy and with higher order interaction energies.
(iii) Detailed analysis of the fourth-order terms, namely the interrelation of the contributions which arise from the double excitations, quadruple excitations and the renormalization term. In this analysis we use the separation of contributions into the exclusion-principle violating (EPV) terms (more properly denoted as conjoint, CJ, terms) and non-EPV or disjoint (DJ) terms, described in our previous articles [11–13]. This last item is of special interest from the methodological point of view, because the mentioned analysis allows precise comparison of the MB-RSPT up to the fourth order with other methods.

The present work is not intended to compete in accuracy with previous *ab initio* calculations on the He_2 system at least for two obvious reasons. First, we are going to use only a moderately extended basis set and, second, we will not take into account all possible types of excitations from the reference Hartree–Fock (HF) determinant. The most important is the omission of the triple excitations, and, consequently, the omission of the intra-inter-molecular correlation coupling [14], which is not negligible [14–17]. The extensive list of previous publications on the He···He interactions may be found in Silver's work [1] and in the recent book by Hobza and Zahradník [17], where also the careful analysis of various theoretical approaches and their comparison with experiment is presented.

2. The Outline of the Method

The basic principles of MB-RSPT have been described in several excellent reviews [18–21]. We restrict ourselves here only to a short description of the notation and to several notes which are relevant for the interpretation of the present results.

Double excitations in the second, third, fourth, and any higher order are denoted as $E_{\mathrm{D}}^{(2)}, E_{\mathrm{D}}^{(3)}, E_{\mathrm{D}}^{(4)}, \ldots$ The fourth-order term $E_{\mathrm{QR}}^{(4)}$ is the sum of contributions from quadruple excitations, $E_{\mathrm{Q}}^{(4)}$, represented by the non-EPV part of connected fourth order quadruple excitation diagrams and the uncancelled conjoint part of the renormalization term, $E_{\mathrm{R}}^{(4)} = (-E_{\mathrm{D}}^{(2)}S)_{\mathrm{CJ}}$. S is the renormalization factor of the first-order wave function. The remaining fourth-order contributions arise from single and triple excitations. As they both require additional integral transformation and, moreover, the triple excitations we are not able to calculate effectively at present, they will not be investigated. The notation for cumulative contributions is obvious. For example, $E_{\mathrm{D}}^{(2)-(4)} = E_{\mathrm{D}}^{(2)} + E_{\mathrm{D}}^{(3)} + E_{\mathrm{D}}^{(4)}$, $E_{\mathrm{DQR}}^{(2)-(4)} = E_{\mathrm{D}}^{(2)-(4)} + E_{\mathrm{QR}}^{(4)}$, and $E_{\mathrm{DR}}^{(2)-(4)} = E_{\mathrm{D}}^{(2)-(4)} + E_{\mathrm{R}}^{(4)}$. The fourth-order approximation to the configuration interaction with doubly excited configurations (CI-D) is the expression $E_{\mathrm{CI\text{-}D}}^{(2)-(4)} = E_{\mathrm{D}}^{(2)-(4)} - E_{\mathrm{D}}^{(2)}S$. Note, that in $E_{\mathrm{CI\text{-}D}}^{(2)-(4)}$ not only $E_{\mathrm{Q}}^{(4)}$ is missed in comparison to $E_{\mathrm{DQR}}^{(2)-(4)}$, but also the disjoint part of $-E_{\mathrm{D}}^{(2)}S$ remains uncancelled. It should be stressed that just the proper cancellation of the disjoint terms of the renormalization contribution and the disjoint terms of the fourth-order disconnected quadruple excitation diagrams together with the cancellation of all conjoint terms in all fourth order quadruple excitation diagrams [12] lead to the correct linear dependence of the fourth-order MB-RSPT energy on the number of electrons, N. This cancellation is equivalent to the statement that only connected diagrams are to be included in the fourth (and any higher) order of MB-RSPT [22]. Fulfilment of this requirement in the calculations of the interaction energy between two closed shell systems leads automatically to the correct behaviour of the interaction potential at large r, where, in our case, $E(\mathrm{He}_2, r)$ should approach $2E(\mathrm{He})$ i.e. $\Delta E(r \to \infty) = 0$. This property has been referred to as "size consistency" [8, 10, 23, 24]. Both ordinary and MB-RSPT are size consistent, order by order, if in each order all contributions are taken into account. Starting from the fourth order this is not always the case, but even then, some energy expressions are size consistent, if they correspond to the connected diagrams. Obviously, $E_{\mathrm{D}}^{(4)}$ and $E_{\mathrm{QR}}^{(4)}$ as well as $E_{\mathrm{D}}^{(2)-(4)}$ and $E_{\mathrm{DQR}}^{(2)-(4)}$ are size consistent, but $E_{\mathrm{CI\text{-}D}}$ and its fourth-order approximation $E_{\mathrm{CI\text{-}D}}^{(2)-(4)}$ are not. In calculations of the interaction energies by CI-D the size inconsistency is usually removed by the calculation of ΔE as a difference between the energy of the supersystem at the given distance and the energy of the supersystem at large (say $50a_0$) distance. This approach, in addition to the fact that it is not strictly theoretically correct, has also practical disadvantage owing to the necessity of one additional calculation of the energy of the supersystem. Moreover, the counterpoise correction is not easily defined in such an approach [25, 26].

An alternative way to overcome these difficulties is to include the small set of quadruple excitations in the CI expansion using the self-consistent electron pair method [27]. The correct dissociation may be obtained with localized, orthogonal natural orbitals. Unfortunately there is no clear answer to the question of how such optimum orbitals should be chosen [27].

Besides using the supermolecule approach we performed also calculations of the HF dispersion energy E_{DISP}. The method is based on the second-order perturbation theory of intermolecular interactions [28] and allows accounting for only the intersystem correlation. We followed the procedure of Kochanski [29], using exclusively the Møller–Plesset partitioning.

3. Results and Discussion

In all calculations we have used the $(6s2p1d)$ Gaussian basis contracted to $[4s2p1d]$, with exponents of p-function 1.2 and 0.3 and complete set of d-functions with exponents 0.8 [30–32]. Energy contributions for the He atom are presented in Table 1. Interaction energies for five interatomic distances r are collected in Table 2.

The ΔE_{SCF} contributions show a shallow spurious minimum at $7a_0$. This was also the case in Silver's calculations with the Slater basis of similar quality. We corrected our SCF values by counterpoise correction [33, 34]. These contributions are denoted as $\Delta E^{\mathrm{CPC}}_{\mathrm{SCF}}$.

Obviously, double excitations represent the most important contribution to the correlation attraction. The dominant part of the effect is obtained already at the second order. This is in accord with other findings for He_2 [1] and also for the $(\mathrm{H}_2)_2$ dimer [35]. More specifically, our $\Delta E^{(2)}_{\mathrm{D}}$ represents about 85% of the most sophisticated value, $\Delta E^{(2)-(4)}_{\mathrm{DQR}}$. The only important correction to $\Delta E^{(2)}_{\mathrm{D}}$ is the third order contribution $\Delta E^{(3)}_{\mathrm{D}}$. Due to the cancellation of the negative $\Delta E^{(4)}_{\mathrm{D}}$ and positive $\Delta E^{(4)}_{\mathrm{QR}}$, the total fourth order contribution $\Delta E^{(4)}_{\mathrm{DQR}}$ is very small. It is of a great practical importance that E_{DISP}, which is relatively simple to calculate, does not differ from the higher order supermolecule calculations too much and thus provides quite good estimation of the correlation contribution to the interaction energy. The main part of the correction to E_{DISP} comes from the third-order effect.

Now let us comment on some approximations at the fourth-order level. As is expected from the theory, both $\Delta E^{(2)-(4)}_{\mathrm{D}}$ and $\Delta E^{(2)-(4)}_{\mathrm{DQR}}$ lead to attractive interaction energies and approach zero with increasing r. In spite of this, using the $\Delta E^{(2)-(4)}_{\mathrm{D}}$ expression for the calculations of the interaction energies is not free of the methodological problems. In this expression the term $E^{(4)}_{\mathrm{R}}$ for the subsystems and both $E^{(4)}_{\mathrm{R}}$ and $E^{(4)}_{\mathrm{Q}}$ for the supersystem are omitted. However, the energy $E^{(2)-(4)}_{\mathrm{D}}$ is incorrect for two-electron systems. In this case, the fourth order renormalization term $E^{(4)}_{\mathrm{R}}=(-E^{(2)}_{\mathrm{D}}S)_{\mathrm{CJ}}\equiv(-E^{(2)}_{\mathrm{D}}S)$ must be included together with $E^{(4)}_{\mathrm{D}}$ for the correct representation of double excitations. Fortunately, in the calculation of the interaction energy the simultaneous omission of both the above mentioned contributions, $\Delta E^{(4)}_{\mathrm{R}}$ and $\Delta E^{(4)}_{\mathrm{Q}}$, does not matter. We can see from Table 2, that $\Delta E^{(4)}_{\mathrm{R}}$ is cancelled by $\Delta E^{(4)}_{\mathrm{Q}}$, so that $\Delta E^{(4)}_{\mathrm{QR}}$ is quite small and $\Delta E^{(2)-(4)}_{\mathrm{D}}$ agrees with $\Delta E^{(2)-(4)}_{\mathrm{DQR}}$ quite well. The approximate cancellation between $\Delta E^{(4)}_{\mathrm{R}}$ and $\Delta E^{(4)}_{\mathrm{Q}}$ seems to resemble the cancellation between energy components $E^{(4)}_{\mathrm{R}}$ and $E^{(4)}_{\mathrm{Q}}$ which is usual in larger molecules [12, 13]. We stress however that for the He_2 supersystem the individual components $E^{(4)}_{\mathrm{R}}$ and $E^{(4)}_{\mathrm{Q}}$ differ considerably ($E^{(4)}_{\mathrm{R}}=49.8\times10^{-5}E_h$, $E^{(4)}_{\mathrm{Q}}=-17.5\times10^{-5}\ E_h$ for interatomic distance $r=6a_0$).

Table 1. Energy components of the He atom (E/E_h)

Energy component[a]	
E_{SCF}	−2.861116570
$E_{\mathrm{D}}^{(2)}$	−0.0300858
$E_{\mathrm{D}}^{(3)}$	−0.0050156
$E_{\mathrm{D}}^{(4)}$	−0.0010586
$E_{\mathrm{D}}^{(5)}$	−0.0002473
$E_{\mathrm{D}}^{(6)}$	−0.0000608
$E_{\mathrm{R}}^{(4)} = -E_{\mathrm{D}}^{(2)} S$	0.0001609
$E_{\mathrm{D}}^{(2)\text{–}(4)}$	−0.0361600
$E_{\mathrm{DR}}^{(4)}$	−0.0008977
$E_{\mathrm{CI\text{-}D}}^{(2)\text{–}(4)} = E_{\mathrm{DR}}^{(2)\text{–}(4)}$	−0.0359991
$E_{\mathrm{SCF}} + E_{\mathrm{DR}}^{(2)\text{–}(4)}$	−2.8971157

[a] For defiinitions see text.

Table 2. Contributions to the interaction energy of the He···He system (energies in $E/E_h \times 10^{-5}$, interatomic distances in r/a_0)

Interaction energy contribution[a]	r				
	5.0	5.5	6.0	7.0	10.0
ΔE_{SCF}	11.93	3.25	0.65	−0.18	0.00
$\Delta E_{\mathrm{SCF}}^{\mathrm{CPC}}$	12.41	3.65	1.06	0.09	0.00
E_{DISP}	−7.72	−4.30	−2.51	−0.97	−0.11
$\Delta E_{\mathrm{D}}^{(2)}$	−8.02	−4.53	−2.66	−1.01	−0.11
$\Delta E_{\mathrm{D}}^{(3)}$	−1.08	−0.69	−0.44	−0.18	−0.02
$\Delta E_{\mathrm{D}}^{(4)}$	−0.17	−0.13	−0.09	−0.04	0.00
$\Delta E_{\mathrm{D}}^{(5)}$	−0.02	−0.02	−0.02	−0.01	0.00
$\Delta E_{\mathrm{D}}^{(6)}$	−0.001	−0.004	−0.004	−0.001	0.000
$\Delta(-E_{\mathrm{D}}^{(2)} S)$	32.38	32.31	32.26	32.22	32.19
$\Delta E_{\mathrm{QR}}^{(4)}$	0.23	0.13	0.07	0.03	0.00
$\Delta E_{\mathrm{R}}^{(4)}$	17.66	17.60	17.58	17.55	17.53
$\Delta E_{\mathrm{D}}^{(2)\text{–}(4)}$	−9.28	−5.35	−3.19	−1.23	−0.13
$\Delta E_{\mathrm{CI\text{-}D}}^{(2)\text{–}(4)}$	23.10	26.95	29.07	30.99	32.06
$\Delta E_{\mathrm{CI\text{-}D,\,corr.}}^{(2)\text{–}(4)}$	−9.09	−5.24	−3.11	−1.20	−0.13
$\Delta E_{\mathrm{DR}}^{(2)\text{–}(4)}$	8.38	12.25	14.39	16.32	17.40
$\Delta E_{\mathrm{Q}}^{(4)}$	−17.43	−17.47	−17.51	−17.53	−17.53
$\Delta E_{\mathrm{DQR}}^{(4)}$	0.05	0.00	−0.01	−0.01	0.00
$\Delta E_{\mathrm{DQR}}^{(2)\text{–}(4)}$	−9.05	−5.23	−3.12	−1.20	−0.13
$\Delta E_{\mathrm{SCF}}^{\mathrm{CPC}} + \Delta E_{\mathrm{DQR}}^{(2)\text{–}(4)}$	3.36	−1.58	−2.06	−1.11	−0.13
$\Delta E_{\mathrm{SCF}}^{\mathrm{CPC}} + E_{\mathrm{DISP}}$	4.69	−0.65	−1.45	−0.88	−0.11

[a] For definitions see text.

It is fair to note that using $\Delta E_{\mathrm{D}}^{(2)\text{–}(4)}$ for calculations of the interaction energies is not always satisfactory. For example, in Be_2 dimer (with near degenerate $2s$ and $2p$ orbitals) the inclusion of only double excitations leads to the spurious local minimum at short distances [10, 36]. This minimum may be removed by the inclusion of quadruple excitations and the renormalization term [10, 36]. It is interesting that, owing to the unsatisfactory cancellation between $\Delta E_{\mathrm{R}}^{(4)}$ and $\Delta E_{\mathrm{Q}}^{(4)}$, better results for Be_2 are obtained by $\Delta E_{\mathrm{CI\text{-}D}}$ than by $\Delta E_{\mathrm{D}}^{(2)-(4)}$, although CI-D is not size-consistent [26].

Finally, let us comment on the $\Delta E_{\mathrm{DR}}^{(2)-(4)}$ and $\Delta E_{\mathrm{CI\text{-}D}}^{(2)-(4)}$ potential curves. They both contain the renormalization term $\Delta E_{\mathrm{R}}^{(4)}$ but not $\Delta E_{\mathrm{Q}}^{(4)}$, and they both provide repulsive interaction energy and incorrect long-range behaviour. With $\Delta E_{\mathrm{CI\text{-}D}}^{(2)-(4)}$, which contains the uncancelled $\Delta(-E_{\mathrm{D}}^{(2)}S)_{\mathrm{DJ}}$ contribution, this behaviour is not unexpected. However, $E_{\mathrm{DR}}^{(2)-(4)}$ is generally correctly N-dependent, so that the failure of this energy deserves more careful analysis. We will follow essentially the ideas of Bartlett and Purvis [10, 37]. The starting point is the fact that the contribution $E_{\mathrm{R}}^{(4)}$ in $E_{\mathrm{DR}}^{(4)}$ for the supersystem is obtained from the separation of the $E_{\mathrm{QR}}^{(4)}$ term into $E_{\mathrm{Q}}^{(4)}$ and $E_{\mathrm{R}}^{(4)}$ components and that this separation is not invariant to a unitary transformation among degenerate orbitals. With symmetry adapted orbitals of He_2, the $E_{\mathrm{R}}^{(4)}$ value of the supersystem at large interatomic distance is about three (instead of two) times larger then $E_{\mathrm{R}}^{(4)}$ for the isolated atom:

$$E_{\mathrm{R}}^{(4)}(\mathrm{He}_2) \approx 3E_{\mathrm{R}}^{(4)}(\mathrm{He}). \tag{2}$$

The factor of three follows from the fact that

$$2E_{\mathrm{R}}^{(4)}(\mathrm{He}) \approx E_{\mathrm{QR}}^{(4)}(\mathrm{He}_2) = E_{\mathrm{Q}}^{(4)}(\mathrm{He}_2) + E_{\mathrm{R}}^{(4)}(\mathrm{He}_2) \tag{3}$$

and, from the result of our calculation, that $E_{\mathrm{R}}^{(4)}(\mathrm{He}_2) \approx -3E_{\mathrm{Q}}^{(4)}(\mathrm{He}_2)$. After localization of molecular orbitals of the supersystem, however, we cannot talk about quadruple excitations, which are simultaneous but independent excitations of two electron pairs (just this type of excitations is currently included in the fourth-order MB-RSPT). Instead, these must be viewed as separate double excitations on individual subsystems. Thus, the contribution from $E_{\mathrm{Q}}^{(4)}(\mathrm{He}_2)$ in Eq. (3) will be absorbed into $E_{\mathrm{R}}^{(4)}(\mathrm{He}_2)$ after localization. Then we obtain a correct factor of two in Eq. (2). In other words, with localized orbitals $E_{\mathrm{QR}}^{(4)}(\mathrm{He}_2) = E_{\mathrm{R}}^{(4)}(\mathrm{He}_2) = 2E_{\mathrm{R}}^{(4)}(\mathrm{He})$, $\Delta E_{\mathrm{Q}}^{(4)}$ would be zero and $\Delta E_{\mathrm{DR}}^{(4)}$ would be equivalent to $\Delta E_{\mathrm{DQR}}^{(4)}$.

At this point it is appropriate to mention the supermolecule calculations with the Epstein–Nesbet partitioning. With such a partitioning using canonical orbitals one obtains a repulsion between two helium atoms at the second (and also at the third) order [1, 5, 38] as a consequence of destroyed balance between diagonal contributions, which are investigated via the Hamiltonian shift, and the non-diagonal ones, which are not [1]. As the summation of diagonal ladders includes in some respect also the summation of certain conjoint contributions of the renormalization term through higher orders of MB-RSPT, without investigation of higher excitations, we can find the connection between the failure of the Epstein–Nesbet calculations and the $\Delta E_{\mathrm{DR}}^{(2)-(4)}$ calculations discussed previously. Accordingly, using the localized orbitals one can obtain the correct interaction potential also by the second-order calculations with the Epstein–Nesbet partitioning [5].

The discussion of the incorrect behaviour of the $\Delta E_{\text{CI-D}}^{(2)-(4)}$ interaction potential need not be very lengthy. It is well known that this energy contains not only the previously discussed $(-E_{\text{D}}^{(2)}S)_{\text{CJ}}$ term, but also the $(-E_{\text{D}}^{(2)}S)_{\text{DJ}}$ term, so that it is size-inconsistent. The total $(-E_{\text{D}}^{(2)}S)$ term of the supersystem is four times as large as that for the subsystem and must be removed from ΔE, supermolecule calculations of the interaction energies, we obtained our corrected values $\Delta E_{\text{CI-D, corr}}^{(2)-(4)}$ as a difference

$$\Delta E_{\text{CI-D, corr}}^{(2)-(4)} = \Delta E_{\text{D}}^{(2)-(4)} + [(-E_{\text{D}}^{(2)}S)(\text{He}_2, r) - (-E_{\text{D}}^{(2)}S)(\text{He}_2, r = 50a_0)]. \tag{4}$$

The results are in very good agreement with $\Delta E_{\text{DQR}}^{(2)-(4)}$.

4. Some Comparisons with Other Works

(i) For the near-equilibrium interatomic distance of $6a_0$ we obtained with $\Delta E_{\text{SCF}}^{\text{CPC}} + \Delta E_{\text{DQR}}^{(2)-(4)}$ only about 60% of the experimental [39] or more accurate *ab initio* [40, 41] van der Waals interaction energy. Such an underestimation of the interaction energy follows immediately from the underestimation of the polarizability of the He atom with our basis: it is only about 84% of the experimental one [31]. Silver obtained, with $\Delta E_{\text{D}}^{(2)-(3)}$ in a Slater basis, a much larger interaction energy than was obtained in the present paper, $-5.4E_h$ at $6a_0$. However, this interaction energy is greatly overestimated, probably owing to the great superposition error.

(ii) The difference between two second order quantities, the supersystem interaction energy $\Delta E_{\text{D}}^{(2)}$ and the dispersion energy E_{DISP}, is negative for all internuclear distances. This difference is connected with the fact, that besides the intersystem correlation energy some additional contributions are taken into account in $\Delta E_{\text{D}}^{(2)}$, but not in E_{DISP}. Namely, it is the change in the intrasystem correlation energy and the effects connected with the overlap between orbitals of individual subsystems. For a more detailed discussion of these points see, e.g., Refs. [14, 17, 41, 42]. Since in the supersystem calculations we used canonical orbitals, it is not possible to evaluate the change in the intrasystem correlation energy separately. From the variational calculations of the Liu and McLean [15] (see also the discussion of Hobza and Zahradník [17], it follows that this quantity is positive at the van der Waals minimum and interatomic distances less then $6a_0$, and it is negative at larger distances. On the other hand, perturbation calculations [41] lead to the negative value of $-0.9 \times 10^{-5}\ E_h$ at $r = 5.6a_0$. It should be stressed, however, that the relation between the supermolecule variational and perturbational definitions of the change of the intramolecular correlation energy is not straightforward [41]. The most closely related to our calculation is the comparison of $\Delta E_{\text{CI-SD}}$ and E_{DISP} by Jaszunski et al. [43] for $\text{H}_2\cdots\text{H}_2$. They found E_{DISP} slightly more attractive than $\Delta E_{\text{CI-SD}}$ calculated as $E_{\text{CI-SD}}(\text{H}_2\cdots\text{H}_2, r) - E_{\text{CI-SD}}(\text{H}_2\cdots\text{H}_2, r = 100a_0)$, in contrast to our case. Of course, with our basis, which is not sufficiently extended, the results of the supermolecule calculations may be obscured by the superposition error. Really, after applying the counterpoise correction to $\Delta E_{\text{D}}^{(2)}$ at $6a_0$, we obtained almost exactly $\Delta E_{\text{D}}^{(2)} = E_{\text{DISP}}$, although, in fact, the superposition error was not too large.

(iii) The relative importance of the individual contributions in the perturbation expansion may be also influenced by the basis set. We obtained some experience in this respect in the calculations of ten-electron hydrides [12] and diatomic molecules [13]. In the cited works we have found that the calculated values of the contributions to $E_{\mathrm{DOR}}^{(2)-(4)}$ may vary with the basis set considerably, but the overall picture of their relative importance is not too much basis set dependent. We believe that this is valid also in calculations of energy differences.

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