Many-Orbital Cluster Expansion for the Exchange-Repulsion Nonadditivity in the Interaction of Rare Gas Atoms. The Neon Trimer*

Marek Bulski and Grzegorz Chałasiński

Department of Chemistry, University of Warsaw, Pasteura 1, 02–093 Warsaw, Poland

Nonadditivity of the exchange repulsion for three neon atoms in the equilateral triangle configuration has been calculated in the first-order of the symmetry adapted perturbation theory. The relative nonadditive contribution to the first-order interaction energy has been found to be about twice as small as in the helium trimer. The many-orbital cluster partition of the exchange nonadditivity has been derived. It has been found that in the region of the van der Waals minimum about 95% of the exchange nonadditivity originates from the interaction of the L-shell electrons only. The five-orbital terms as well as terms of an order-higher than S^3 have been found to be negligible. Approximate formulae for evaluation of the exchange repulsion nonadditivity has been proposed and discussed.

Key words: Three-body nonadditivity–Ne_3.

1. Introduction

The three-body interactions proved to be important in determining various properties of noble gases, as the ground state energy of trimers [1], third virial coefficients [2, 3], elastic constants of solids [2, 4].

The total three-body effect can be, by means of symmetry adapted perturbation theory, decomposed into well defined contributions which have clear physical interpretation and can be examined separately [5]. The results for model systems, H_3 [6, 7] and He_3 [8] suggest that for noble gas trimers the most important three-body effects are: the short-range nonadditivity of the first-order exchange interaction and the long-range nonadditivity of the third-order dispersion interaction. For the equilateral triangle configuration the former effect is attractive and dominates at the interatomic distances smaller than R_m – the distance of the van der Waals minimum in the interaction of a pair of atoms. The latter one is repulsive and dominates at the distances greater

---

than R_m. For separations close to R_m both effects are of comparable magnitude. The third-order dispersion nonadditivity may be reliably represented with the aid of the van der Waals coefficients. Even for large atoms they can be calculated quite accurately using semiempirical methods [9]. On the contrary, the nonadditive exchange effects can be obtained only from *ab initio* quantum mechanical calculations. As a consequence, our knowledge of the actual magnitude of these effects in the van der Waals minimum region is limited to a few simplest systems [6–8, 10, 11].

To take into account the nonadditive exchange effect the supermolecular SCF treatment employing the counterpoise method [12] might be considered as the most useful in practical calculations for noble gases [13, 14]. This is because the SCF method allows not only for the first-order nonadditive effects, but for the induction and exchange-induction nonadditivities of the second and higher orders as well. The latter effects proved to be of crucial importance in the case of Be_3 system [11]. However, this is not the case for aggregates of noble gas atoms [8, 14] because of their hard-to-deform spherical distribution of the electronic charge. Moreover, calculations in the framework of the supermolecular SCF approach become very time-consuming and inaccurate for larger systems. One should remember that, since the nonadditive component of the interaction energy is small and is obtained as a difference of much larger numbers, the error may be larger than the effect itself. Taking all these into account it is advantageous in the case of rare gas atoms to evaluate the three-body exchange effect directly, using the perturbation expression for the first-order energy [8]. The important merit of this approach is the possibility of introducing for larger systems well defined and easy to verify approximations [10]. Furthermore the knowledge of the first-order three-body nonadditivity allows us to check and interpret supermolecular variational results (if available) as well as approximate model calculations [15, 16].

It has been demonstrated in [5] that the leading term of the three-body nonadditivity of the first-order exchange repulsion is, for an aggregate of neutral atoms, of order S^3 where S denotes the interatomic overlap integral. In this paper we derive an explicit formula for this leading contribution assuming the wave functions of isolated atoms in the form of single determinants. The result is written in the form of a many-orbital cluster expansion which proved to be very convenient for calculations of the exchange effects [17, 18]. The advantages of the many-orbital expansion are: clear physical interpretation of the various exchange contributions and possibility of introducing approximate formulae arising if one neglects some of the many-orbital terms and calculates approximately the other ones.

The derived formula as well as the exact expression of Ref. [8] have been used to calculate the three-body exchange nonadditivity for the equilateral triangle configuration of Ne_3 at the interatomic separations ranging from 3 a.u. to 7 a.u. and assuming Hartree–Fock wave function for the neon atom. The Ne_3 system is the simplest one composed of many-electron and many–shell atoms, which,

in contrast to beryllium atoms, have hard-to-deform spherical distribution of charge. Previous SCF calculations of the nonadditive effect in Ne_3 [19] have been limited to very short interatomic distances up to 3.2 a.u., thereby give no information for the physically significant distance of nearest neighbours in the neon crystal [2]. This distance is close to R_m and equals approximately 5.8 a.u. [2].

We have performed many-orbital and many-shell analysis of the results and the above mentioned approximate expressions are proposed and discussed. A comparison of the first-order three-body effect with two-body one as well as with the Axilrod–Teller triple-dipole energy has been also made for H_3, He_3 and Ne_3.

2. Nonadditivity of the First-Order Exchange Repulsion and Many-Orbital Cluster Expansion Thereof

The first-order energy for three interacting closed-shell systems in the symmetry adapted perturbation theory is defined as

$$E_{int}^{(1)} = \frac{\langle \Phi_A \Phi_B \Phi_C | \mathscr{A} V | \Phi_A \Phi_B \Phi_C \rangle}{\langle \Phi_A \Phi_B \Phi_C | \mathscr{A} | \Phi_A \Phi_B \Phi_C \rangle} \tag{1}$$

where $\mathscr{A}$ is the antisymmetrizer for all electrons of complex ABC, Φ_A, Φ_B, Φ_C denote the determinantal wave functions of the systems A, B, C – respectively, and V is the operator of intermolecular interaction, which may be conveniently written in the form

$$V = V^{AB} + V^{BC} + V^{CA} \tag{2}$$

where

$$V^{AB} = \sum_{s \in A} \sum_{t \in B} v^{AB}(st) \tag{3}$$

and $v^{AB}(st)$ is a generalized two-electron potential [17]. For the interaction of neutral atoms it is defined as

$$v^{AB}(st) = R_{AB}^{-1} - r_{At}^{-1} - r_{Bs}^{-1} + r_{st}^{-1} \tag{4}$$

where R_{AB} is the internuclear separation and r_{At}, r_{Bs} and r_{st} are distances between the nuclei and electrons specified by the subscripts A, B, s and t.

The first-order interaction energy (1) can be separated into Coulomb and exchange contributions

$$E_{int}^{(1)} = Q + E_{exch}^{(1)} \tag{5}$$

where $Q = \langle \Phi_A \Phi_B \Phi_C | V | \Phi_A \Phi_B \Phi_C \rangle$ and the exchange contribution is defined as the difference $E_{int}^{(1)} - Q$. One can easily show that the Coulomb energy is pair-wise additive and that the exchange contribution $E_{exch}^{(1)}$ can be decomposed into two- and three-body parts, $E_{exch}^{(1)}(2, 3)$ and $E_{exch}^{(1)}(3, 3)$, respectively, which

are defined as follows

$$E^{(1)}_{\text{exch}}(2, 3) = \lim_{R_{\text{CA}}, R_{\text{BC}} \to \infty} E^{(1)}_{\text{exch}} + \lim_{R_{\text{AB}}, R_{\text{CA}} \to \infty} E^{(1)}_{\text{exch}} + \lim_{R_{\text{AB}}, R_{\text{BC}} \to \infty} E^{(1)}_{\text{exch}} \tag{6}$$

and

$$E^{(1)}_{\text{exch}}(3, 3) = E^{(1)}_{\text{exch}} - E^{(1)}_{\text{exch}}(2, 3) \tag{7}$$

For the neutral atoms the first non-vanishing contribution to the three-body nonadditivity of the exchange energy is of the third-order in the interatomic overlap integrals [5]. To define explicitly this contribution one should extract from $\mathscr{A}$ in Eq. (1) the operators interchanging coordinates of electrons among the interacting systems and classify them with respect to powers of S, using arguments similar to those of Ref. [20]. Then, the two-body contributions and terms of order higher than S^3 can be removed and the result may be written as follows

$$E_{\text{exch}}(3, 3) = E^{\text{AB(C)}}_{\text{exch}}(3, 3) + E^{\text{BC(A)}}_{\text{ech}}(3, 3) + E^{\text{CA(B)}}_{\text{exch}}(3, 3) \tag{8}$$

where

$$E^{\text{AB(C)}}_{\text{exch}}(3, 3) = \langle \Phi_{\text{A}} \Phi_{\text{B}} \Phi_{\text{C}}| \ V^{\text{AB}}(Q^{\text{AB(C)}} - \langle Q^{\text{AB(C)}} \rangle) |\Phi_{\text{A}} \Phi_{\text{B}} \Phi_{\text{C}} \rangle \tag{9}$$

The operator $Q^{\text{AB(C)}}$ is defined:

$$Q^{\text{AB(C)}} = \mathscr{P}^{\text{AC}} + \mathscr{P}^{\text{BC}} + \mathscr{P}^{\text{ABC}} + \mathscr{P}^{\text{BCA}} \tag{10}$$

$$\mathscr{P}^{\text{AC}} = - \sum_{s \in \text{A}} \sum_{r \in \text{C}} P_{sr} \tag{11}$$

and

$$\mathscr{P}^{\text{ABC}} = \sum_{s \in \text{A}} \sum_{t \in \text{B}} \sum_{r \in \text{C}} P_{st} P_{tr} \tag{12}$$

where P_{sr} interchanges the coordinates of sth and rth electrons and $\langle Q^{\text{AB(C)}} \rangle$ is calculated with $\Phi_{\text{A}} \Phi_{\text{B}} \Phi_{\text{C}}$.

It is seen from Eqs. (9)–(12) that $E^{\text{AB(C)}}_{\text{exch}}$ may be regarded as a modification of the two-body interaction between A and B caused by the effect of exchanging electrons with C atom. We notice that to obtain this term it is sufficient to consider the operators interchanging at most one electron of each centre at a time. From this point of view $E_{\text{exch}}(3, 3)$ may be envisaged as arising from single-electron exchanges only.

It is simple to evaluate formula (9) for one and two-electron systems; for larger systems, however, the algebra becomes tedious and involved. In a general case, it seems easier to express the total $E^{(1)}_{\text{int}}$ in terms of orbitals [8] and, after expanding it in powers of S, to extract the three-body terms of order S^3. The

result can be written in the form of a many-orbital cluster expansion

$$E_{\text{exch}}^{\text{AB(C)}}(3,3) = \sum_{i \in A} \sum_{j \in B} \sum_{m \in C} \varepsilon_{ijm}^{\text{AB(C)}}$$

$$+ \sum_{\substack{i,k \in A \\ i<k}} \sum_{j \in B} \sum_{m \in C} \varepsilon_{ikjm}^{\text{AAB(C)}} + \sum_{i \in A} \sum_{\substack{j,l \in B \\ j<l}} \sum_{m \in C} \varepsilon_{ijlm}^{\text{ABB(C)}} + \sum_{\substack{i,k \in A \\ i<k}} \sum_{\substack{j,l \in B \\ j<l}} \sum_{m \in C} \varepsilon_{ikjlm}^{\text{AABB(C)}} \quad (13)$$

where, for instance, the symbol $\varepsilon_{ikjm}^{\text{AAB(C)}}$ indicates that the corresponding four-orbital contribution depends only on the ith and kth orbitals of system A, jth orbital of system B and mth orbital of system C. The contributions $\varepsilon_{ikjm}^{\text{AAB(C)}}$, $\varepsilon_{ijlm}^{\text{ABB(C)}}$ and $\varepsilon_{ikjlm}^{\text{AABB(C)}}$ are defined to be symmetric with respect to the interchange of indices i and k or l and j, and can be obtained by s symmetrization of the "primitive" quantities: $\tilde\varepsilon_{ikjm}^{\text{AAB(C)}}$, $\tilde\varepsilon_{ijlm}^{\text{ABB(C)}}$ and $\tilde\varepsilon_{ikjlm}^{\text{AABB(C)}}$:

$$\varepsilon_{ikjm}^{\text{AAB(C)}} = \tilde\varepsilon_{ikjm}^{\text{AAB(C)}} + \tilde\varepsilon_{kijm}^{\text{AAB(C)}} \quad (14)$$

or

$$\varepsilon_{ikjlm}^{\text{AABB(C)}} = \tilde\varepsilon_{ikjlm}^{\text{AABB(C)}} + \tilde\varepsilon_{kijlm}^{\text{AABB(C)}} + \tilde\varepsilon_{ikljm}^{\text{AABB(C)}} + \tilde\varepsilon_{kiljm}^{\text{AABB(C)}} \quad (15)$$

The explicit expressions for the many-orbital contributions to $E_{\text{exch}}(3,3)$ are as follows:

$$\begin{aligned}
\varepsilon_{ijm}^{\text{AB(C)}} = &\, 2\langle a_i a_i | \, v_{12} \, | a_i b_j \rangle S_{jm}^{bc} S_{mi}^{ca} + 2\langle a_i b_j | \, v_{12} \, | b_j b_j \rangle S_{im}^{ac} S_{mj}^{cb} \\
&+ 4\langle a_i b_j | \, v_{12} \, | a_i b_j \rangle S_{ij}^{ab} S_{jm}^{bc} S_{mi}^{ca} \\
&+ 2\langle a_i b_j | \, v_{12}(1-2P_{12}) c_m a_i \rangle S_{jm}^{bc} \\
&+ 2\langle a_i b_j | \, v_{12}(1-2P_{12}) b_j c_m \rangle S_{im}^{ac} \\
&- 2\langle a_i b_j | \, v_{12} \, | c_m b_j \rangle S_{ij}^{ab} S_{jm}^{bc} \\
&- 2\langle a_i b_j | \, v_{12} \, | a_i c_m \rangle S_{im}^{ac} S_{ji}^{ba} \quad (16)
\end{aligned}$$

$$\begin{aligned}
\tilde\varepsilon_{ikjm}^{\text{AAB(C)}} = &\, 4\langle a_i a_k | \, v_{12} \, | a_i b_j \rangle S_{jm}^{bc} S_{mk}^{ca} - 2\langle a_k a_i | \, v_{12} \, | a_i b_j \rangle S_{jm}^{bc} S_{mk}^{ca} \\
&+ 2\langle a_i b_j | \, v_{12} \, | a_k b_j \rangle [S_{jm}^{bc} S_{ij}^{ab} S_{mk}^{ca} + S_{jm}^{bc} S_{im}^{ac} S_{jk}^{ba}] \\
&- 2\langle a_i b_j | \, v_{12} \, | a_k c_m \rangle S_{im}^{ac} S_{jk}^{ba} \quad (17)
\end{aligned}$$

$$\tilde\varepsilon_{ikjlm}^{\text{AABB(C)}} = 2\langle a_i b_l | \, v_{12} \, | a_k b_j \rangle [S_{ij}^{ab} S_{lm}^{bc} S_{mk}^{ca} + S_{im}^{ac} S_{mj}^{cb} S_{lk}^{ba}] \quad (18)$$

where the occupied orbitals of systems A, B, C are denoted by a_i, a_k, b_j, b_l and c_m respectively, $S_{ij}^{ab} = \langle a_i | b_j \rangle$, $v_{12} = v^{ab}(12)$ and the expression for $\tilde\varepsilon_{ijlm}^{\text{ABB(C)}}$ can be obtained from Eq. (17) by substituting b_l for a_k, v_{21} for v_{12} and interchanging a_i and b_j.

It is important to stress that the many-orbital cluster expansion given by Eq. (13) enables us to express $E_{\text{exch}}(3,3)$ also in terms of shells or other subgroups of orbitals. Moreover, a clear physical interpretation may be associated with particular terms in Eq. (13). For example the sum of three-orbital contributions to $E_{\text{exch}}(3,3)$ for a given i, j, m: $\varepsilon_{ijm}^{\text{AB(C)}} + \varepsilon_{jmi}^{\text{BC(A)}} + \varepsilon_{mij}^{\text{CA(B)}}$, is identical with the expression for $E_{\text{exch}}(3,3)$ in the interaction of three helium-like systems. Therefore the above three-orbital contribution to $E_{\text{exch}}(3,3)$ can be interpreted

as a result of three-body nonadditive exchange interactions among orbitals: a_i of A, b_j of B and c_m of C. The higher many-orbital terms have a similar interpretation. For instance, the sum: $\varepsilon_{ikjm}^{AAB(C)} + \varepsilon_{ikmj}^{AAC(B)}$, is identical with the expression for that part of $E_{exch}(3, 3)$ which, for the system composed of beryllium-like atom and two helium-like atoms, is not due to the three-orbital interactions. It may be thus considered as resulting from the four-orbital ones: a_i, a_k of beryllium, b_j of helium B and c_m of helium C.

Finally, we would like to comment on the terms formally of order S^2 which are present in Eq. (16) (the second component of the fourth and fifth terms). It is easy to show, by using the Mullikan approximation and the multipole expansion of the $v^{AB}(st)$ potential, that for neutral atoms the S^2 component of one- and two-electron integrals cancel each other and that the leading contribution is of the order S^3. Similarly, the expression for $\tilde{\varepsilon}_{ilkm}^{AAB(C)}$ lacks the term formally of order S^2: $4\langle a_i b_k | v_{12} | a_i b_k \rangle S_{im}^{ac} S_{ml}^{ca}$ that can be similarly proved to be of order S^4. This fact was disregarded by Williams, Schaad and Murrell [21] who used solely the discussed above S^2 terms to approximate $E_{exch}^{(1)}(3, 3)$. In fact these terms give incorrect sign of the first-order three-body nonadditivity of rare-gas trimers as may be proved by explicit calculations of the relevant integrals (see Ref. [22] and Sec. 3). It should be stressed however, that for ions or molecules the cancellation of S^2 contributions does not occur and the terms discussed above dominate the three-body nonadditivity [23].

3. Numerical Calculations of the Three-Body Exchange Effect in the Neon Trimer

The calculations of the first-order three-body nonadditivity and of its components have been performed for the equilateral triangle configuration of Ne_3. We have used (4/4/4) and (6/8/8) Gaussian representations (see Ref. [18]) of Clementi's SCF orbitals for the neon atom [24]. The values of $E_{exch}^{(1)}(3, 3)$ obtained with both wave functions, for interatomic distances ranging from 3 a.u. to 7 a.u., are displayed in Table 1. The results obtained with the (6/8/8)

Table 1. A comparison of the values of the first-order nonadditivity $E_{exch}^{(1)}(3, 3)$ obtained with various Gaussian representations of Clementi's SCF orbitals [24] for the Ne_3 system in the equilateral triangle configuration. The energy and the interatomic distance R are expressed in atomic units

R	(4/4/4)	(6/8/8)	$E^{(1)}(3, 3) - E_{exch}(3, 3)$[a]	S^2 terms[a]
3.0	$-2.0863 (-2)$	$-2.1550 (-2)$	$+2.51 (-3)$	$+1.2438 (-2)$
4.0	$-7.2587 (-4)$	$-6.9699 (-4)$	$+2.08 (-5)$	$+3.1412 (-4)$
5.0	$-2.4516 (-5)$	$-2.0568 (-5)$	$-5.85 (-8)$	$+7.3939 (-6)$
5.5	$-4.0276 (-6)$	$-3.5145 (-6)$	$-2.77 (-8)$	$+1.1399 (-6)$
6.0	$-6.3237 (-7)$	$-5.9505 (-7)$	$-5.82 (-9)$	$+1.7484 (-7)$
7.0	$-1.6445 (-8)$	$-1.6658 (-8)$	$-1.62 (-10)$	$+4.0755 (-9)$

[a] Results obtained with the (6/8/8) function.

wave function may be considered, on the basis of the two-body energy calculations for Ne_2 [18], as accurate within a few percent. From the practical point of view it is also important to point that the rather poor (4/4/4) fit gives a reasonable estimation of $E_{exch}^{(1)}(3, 3)$ within considered region.

To visualize the role of terms of order higher than S^3 we have listed the difference $E_{exch}^{(1)}(3, 3) - E_{exch}(3, 3)$ in the last but one column of Table 1. One can see that this effect is negligible in the region 4-7 a.u. accounting for from +3% to −1% of $E_{exch}^{(1)}(3, 3)$. At $R = 3$ a.u., however, its contribution increases to +11%. This indicates that the expansion in powers of S is no longer useful at this and smaller distances. In addition, for $R \leqslant 3$ a.u. the neglect of induction-type effects is not justified [14].

In the last column of Table 1 the contribution from all the terms formally of order S^2, discussed in Sec. 2, is also reported. We see that its sign differs from that of $E_{exch}^{(1)}(3, 3)$ within the region under consideration.

In Table 2 we report the multi-shell partitioning of $E_{exch}(3, 3)$. The notation is a direct generalization of that adopted in Ref. [18]. The inter-shell contributions not listed in Table 2 are less than 0.01% of $E_{exch}^{(1)}(3, 3)$. The results show

Table 2. A comparison of the largest individual inter-shell contributions to the first-order nonadditivity for the Ne_3 system in equilateral triangle configuration (for the (6/8/8) wave function). The interatomic distance R is expressed in atomic units, all other quantities in percent

R	$E_{LLL}^{ABC}/E_{exch}(3, 3)$	$E_{KLLL}^{AABC}/E_{exch}(3, 3)$	$E_{KLL}^{ABC}/E_{exch}(3, 3)$
4.0	94.73	4.91	0.72
5.0	96.04	3.43	0.53
5.5	96.64	2.92	0.44
6.0	97.12	2.51	0.37
7.0	97.79	1.92	0.29

that, for all the distances considered, the first-order nonadditivity can be approximated with the accuracy greater than 94% by the interaction of outer shells only. Inclusion of $KL-L-L$ type terms (analogous to $KL-L$ in Ne_2) leads to 99% accuracy. An orbital analysis of the predominant many-shell contributions seems to be also of interest. The $E_{LLL}^{AB(C)}$ term can be separated into components originating from three-, four- and five-orbital contributions:

$$E_{LLL}^{AB(C)} = E_{LLL}^{AB(C)}(3) + E_{LLL}^{AB(C)}(4) + E_{LLL}^{AB(C)}(5) \qquad (19)$$

In the same way we can decompose the second largest term $-E_{KLLL}^{AAB(C)}$

$$E_{KLLL}^{AAB(C)} = E_{KLLL}^{AAB(C)}(4) + E_{KLLL}^{AAB(C)}(5) \qquad (20)$$

The contributions of particular terms to $E_{LLL}^{AB(C)}$ and $E_{KLLL}^{AAB(C)}$ have been compared in Table 3. On the basis of the many-orbital analysis of the two-body E_{LL}^{AB} term (see Table 5 of Ref. [18]) one can expect that the largest contribution to $E_{LLL}^{AB(C)}$ would result from the four-orbital interactions and that the

Table 3. A comparison of many-orbital contributions to the nonadditive interaction of L-shells as well as two L-shells with KL shells (for the (6/8/8) wave function) for the Ne_3 system in the equilateral triangle configuration. The interatomic distance R is expressed in atomic units, all other quantities are multiplied by 10^2

R	4.0	5.0	5.5	6.0	7.0
$E_{LLL}(3)/E_{LLL}^{ABC}$	-55.10	-39.25	-32.74	-27.12	-17.73
$E_{LLL}(4)/E_{LLL}^{ABC}$	158.74	141.05	134.05	128.09	118.29
$E_{LLL}(5)/E_{LLL}^{ABC}$	-3.64	-1.80	-1.31	-0.97	-0.56
$E_{KLLL}(4)/E_{KLLL}^{AABC}$	100.62	100.39	100.32	100.27	100.19
$E_{KLLL}(5)/E_{KLLL}^{AABC}$	-0.62	-0.39	-0.32	-0.27	-0.19

five-orbital terms would be negligible. This supposition is entirely confirmed by the results of Table 3. However, the relative role of three- and four-orbital terms is different as compared to the relative role of two- and three-orbital contributions for Ne_2: $E_{LLL}^{AB(C)}(4)$ is from 1.6 to 1.2 times greater than $E_{LLL}^{AB(C)}$ itself and cannot provide us a useful approximation of the latter. Moreover, $E_{LLL}^{AB(C)}(3)$ is of the opposite sign to $E_{LLL}^{AB(C)}(4)$. We notice that the role of $E_{LLL}^{AB(C)}(3)$ rapidly decreases with increasing R. A similar analysis of the $E_{KLLL}^{AAB(C)}$ contribution (the two last rows of Table 3) shows, that only the four-orbital terms are needed to reproduce it accurately.

In Ref. [18] it was shown that the two-body contribution E_{LL}^{AB} may be quite accurately represented by the sum of three largest three-orbital components. We have tried to generalize the respective approximate formula (16) of Ref. [18]. The third atom C has been fixed on the x-axis (see Fig. 1) going through the midpoint of A–B separation. Next we have replaced in Eq. (16) of Ref. [18] the three-orbital components by the four-orbital ones and at the centre C we have situated the $2p_x$ orbital, which is supposed to give the largest overlap with orbitals at A and B centres. The resulting approximate formula for the
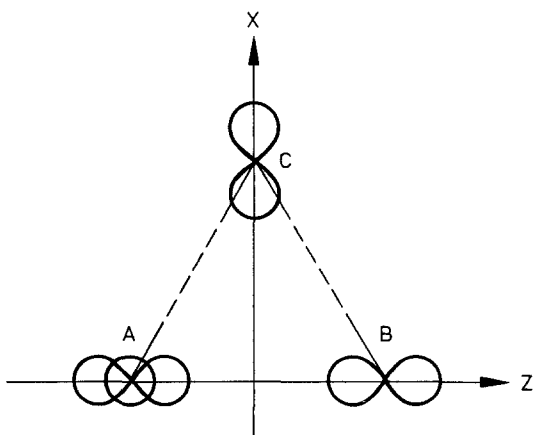

Fig. 1.

Table 4. A comparison of various four-orbital contributions to the first-order nonadditive interaction of L shells and to the three-body nonadditive energy $-E^{(1)}_{exch}(3,3)$ in equilateral triangle configuration (for the (6/8/8) wave function). The interatomic distance R is expressed in atomic units, all other quantities in percent

R	4.0	5.0	5.5	6.0	7.0
$2\varepsilon^{AAB(C)}_{zszx}/E^{AB(C)}_{LLL}$	34.68	37.56	38.48	39.08	39.56
$2\varepsilon^{AAB(C)}_{xszx}/E^{AB(C)}_{LLL}$	21.16	20.92	20.40	19.70	18.06
$2\varepsilon^{AAB(C)}_{xzzx}/E^{AB(C)}_{LLL}$	13.50	15.86	16.94	17.86	19.38
$2\varepsilon^{AAB(C)}_{yszx}/E^{AB(C)}_{LLL}$	18.56	18.60	18.24	17.72	16.38
$2\varepsilon^{AAB(C)}_{yzzx}/E^{AB(C)}_{LLL}$	12.12	14.54	15.68	16.68	18.34
$E^{AB(C)}_{approx}(4)/E^{AB(C)}_{LLL}$	100.02	107.48	109.74	110.04	112.26
$3E^{AB(C)}_{approx}(4)/E^{(1)}(3,3)$	96.34	102.94	105.19	106.80	108.19

AB side of Ne_3 triangle may be written in the form:

$$E^{AB(C)}_{approx} = 2(\varepsilon^{AAB(C)}_{zszx} + \varepsilon^{AAB(C)}_{xszx} + \varepsilon^{AAB(C)}_{xzzx} + \varepsilon^{AAB(C)}_{yszx} + \varepsilon^{AAB(C)}_{yzzx}) \qquad (21)$$

where s, x, y, z denote $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals, respectively. The relative contributions to $E^{AB(C)}_{LLL}$ from individual terms in Eq. (21) have been compared in Table 4. In the last row of this table we have domonstrated the usefulness of the formula (21) to estimate the three-body exchange nonadditivity. The results are encouraging – the resulting error is less than 8% in the region considered. It is, however, important to remark that this result is due to the cancellation of some of four-orbital terms with the three-orbital ones and not to the smallness of the latter (cf Table 3).

Concluding the discussion of this section we see that for the equilateral triangle configuration it is possible to introduce various simplifications in the evaluation of the three-body nonadditivity of the first-order energy:

1. Neglect of terms of order higher than S^3.
2. Neglect of contributions from inner-shell orbitals.
3. Neglect of five-orbital contributions.
4. Use of approximate algorithms of the type of Eq. (21).
5. Calculation of some less important terms using poorer representations of Hartree–Fock orbitals.

The above approximations can substantially simplify the evaluation of the three-body exchange effects for clusters of larger rare gas atoms. The work in this direction is in progress in our laboratory.

4. Exchange Nonadditivity versus Two-Body First-Order Energy and Triple-Dipole Effect. Comparison of H_3, He_3 and Ne_3

In Table 5 we have collected the values of the relative nonadditivity $\varepsilon_3 = E^{(1)}_{exch}(3,3)/E^{(1)}(2,3)$ for the equilateral triangle configuration of H_3, He_3 and Ne_3. It is seen that for the distances corresponding to the van der Waals

Table 5. A comparison of the values of the relative nonadditivity ε_3, for hydrogen, helium and neon trimers in equilateral triangle configuration. The interatomic distance R is expressed in atomic units, ε_3 in percent

R	$\varepsilon_3(H_3)$[a]	$\varepsilon_3(He_3)$[c]	$\varepsilon_3(Ne_3)$[d]
3.0	−20.53	−10.39	−5.34
4.0	−14.53	−4.38	−2.72
5.0	−8.99	−1.61	−0.90
5.5	—	—	−0.51
6.0	−5.03	−0.55	−0.29
7.0	−2.62	−0.19	−0.09
8.0	−1.29[b]		
10.0	−0.25[b]		

[a] Ref. [6]. [b] Ref. [7]. [c] Ref. [8]. [d] Present work.

minima ε_3 for Ne_3 is less than 1% and is twice and thrice as small as for He_3 and H_3 respectively. Our results confirm the prediction of Leś [25] based on the effective electron model [15].

In order to estimate the actual magnitude of the total three-body nonadditivity for the above trimers we have compared in Table 6 the values of $E_{exch}^{(1)}(3,3)$

Table 6. A comparison of the first-order and triple-dipole nonadditivities for hydrogen, helium and neon trimers in equilateral triangle configurations. The energies and the interatomic distance R are expressed in atomic units

R	H_3		He_3		Ne_3	
	$E_{exch}^{(1)}(3,3)$[a]	$E_{ddd}^{(3)}(3,3)$[c]	$E_{exch}^{(1)}(3,3)$[d]	$E_{ddd}^{(3)}(3,3)$[e]	$E_{exch}^{(1)}(3,3)$[f]	$E_{ddd}^{(3)}(3,3)$[e]
3.0	−2.306 (−2)	7.829 (−5)	−4.720 (−3)	1.0 (−4)	−2.155 (−2)	8.9 (−4)
4.0	−3.835 (−3)	2.550 (−5)	−1.930 (−4)	7.8 (−6)	−6.970 (−4)	6.7 (−5)
5.0	−6.914 (−4)	7.766 (−6)	−6.403 (−6)	1.045 (−6)	−2.057 (−5)	8.976 (−6)
5.5	—	—	—	—	−3.515 (−6)	3.807 (−6)
6.0	−5.838 (−5)	2.236 (−6)	−1.914 (−7)	2.026 (−7)	−5.951 (−7)	1.740 (−6)
7.0	−5.803 (−6)	6.643 (−7)	−5.364 (−9)	5.060 (−8)	−1.666 (−8)	4.344 (−7)
8.0	−5.336 (−7)[b]	2.139 (−7)	−1.484 (−10)	1.521 (−8)		
10.0	−3.619 (−9)[b]	2.966 (−8)				

[a] Ref. [6], [b] Ref. [7], [c] Ref. [26] – nonexpanded triple-dipole energy, [d] Ref. [8], [e] calculated with C_9 of Ref. [9], [f] Present work

calculated in the previous section and the triple-dipole energy, $E_{ddd}^{(3)}(3,3)$. The reported values of $E_{ddd}^{(3)}(3,3)$ for H_3 have been calculated by O'Shea and Meath [26] and allow for the charge overlap effects. For He_3 and Ne_3 the triple-dipole terms have been calculated in the multipole approximation using for the van der Waals coefficients C_9 the values of Tang et al. [9]. A similar approximation for the triple-dipole effect for H_3 gives in the region of the van der Waals minimum results in error of 4% at $R = 8$ a.u. and 11% at $R = 7$ a.u. Thus, it seems reasonable to assume that for He_3 and Ne_3 the triple-dipole interaction

is highly overestimated only for $R < 5$ a.u. For these distances we report only two figures of the approximate results, solely to illustrate the dominant role of $E_{\text{exch}}^{(1)}(3, 3)$.

Perusal of the results of Table 6 leads to the interesting conclusion that the absolute value of $E_{\text{exch}}^{(1)}(3, 3)$ increases substantially slower than $E_{\text{ddd}}^{(3)}(3, 3)$ with increasing size of rare gas atoms in the trimer. For Ne_3, within the whole investigated region, the former effect is about 3 times larger, whereas the latter about 9 times larger than in the case of He_3 system. Another important conclusion is that the region where $E_{\text{exch}}^{(1)}(3, 3)$ and $E_{\text{ddd}}^{(3)}(3, 3)$ are of comparable magnitude is, for all the investigated systems, the van der Waals minimum region. In our comparison we have neglected the higher terms in the multipole expansion of $E^{(3)}(3, 3)$ as well as the fourth- and higher-order three-body dispersion terms. It has been argued, however, that their contribution is substantially smaller than $E_{\text{ddd}}^{(3)}(3, 3)$, due to a fortuitous cancellation of repulsive and attractive effects [4]. On the other hand, we also expect, on the basis of the H_3 example, that the exchange-dispersion nonadditive effect does not modify the total exchange effect considerably: at $R = 8$ a.u. it has been estimated to be about 10 times smaller than $E_{\text{exch}}^{(1)}(3, 3)$ [7]. In addition a cancellation of the induction-type effects, disregarded in our treatment, can be expected. Finally, on the basis of calculations for helium dimer [27] the intraatomic electron correlation effects are supposed to be not very important.

The above analysis suggests that the evaluation of $E_{\text{exch}}^{(1)}(3, 3)$, and $E_{\text{ddd}}^{(3)}(3, 3)$ can provide us with reliable information about the magnitude of the total nonadditivity of interaction within a wide range of interatomic distances. The neglected contributions may be, however, essentially more important at the distances where $E_{\text{exch}}^{(1)}(3, 3)$ and $E_{\text{ddd}}^{(3)}(3, 3)$ nearly cancel each other. This fact should be borne in mind in studies of the nodal structure [28] of the total nonadditive effect.

References

1. Bruch, L. W., McGee, I. J.: J. Chem. Phys. **59**, 409 (1973)
2. Barker, J. A.: in: Rare Gas Solids, Vol. 1, Klein, M. L., Venables, J. A., Ed. Academic Press 1976 and Refs. therein
3. Leś, A.: Chem. Phys. Letters **37**, 399 (1976)
4. Bell, R. J., Zucker, I. J.: in: Rare Gas Solids, Vol. 1, Klein, M. L., Venables, J. A.; Ed. Academic Press (1976) and Refs. therein
5. Kołos, W.: in: The World of Quantum Chemistry, Daudel, R., Pullman, B., Ed. Dordrecht-Holland (1974)
6. Kołos, W., Leś, A.: Chem. Phys. Letters **14**, 167 (1972)
7. Jeziorski, B.: Ph. D. Thesis., Warsaw 1974

 8. Jeziorski, B., Bulski, M., Piela, L.: Intern. J. Quantum Chem. **10,** 281 (1976)
 9. Tang, K. T., Norbeck, J. M., Certain, P. R.: J. Chem. Phys. **64,** 3063 (1976)
10. Bulski, M.: Mol. Phys. **29,** 1171 (1975)
11. Kołos, W., Nieves, F., Novaro, O.: Chem. Phys. Letters **41,** 431 (1976)
12. Boys, S. F., Bernardi, F.: Mol. Phys. **19,** 553 (1970)
13. Bulski, M., Chałasiński, G.: Theoret. Chim. Acta (Berl.) **44,** 399 (1977)
14. Bulski, M.: to be published
15. Kołos, W., Leś, A.: Intern. J. Quantum Chem. **6,** 1101 (1972)
16. Kim, Y. S.: Phys. Rev. A, **11,** 796, 804 (1975)
17. Chałasiński, G., Jeziorski, B.: Theoret. Chim. Acta (Berl.) **46,** 277 (1977)
18. Bulski, M., Chałasiński, G., Jeziorski, B.: Theoret. Chim Acta (Berl.) **52,** 91 (1979)
19. Novaro, O., Nieves, F.: J. Chem. Phys. **65,** 1109 (1976) and Refs. therein
20. Murrell, J. N., Randič, M., Williams, D. R.: Proc. Roy. Soc. London **A284,** 566 (1965);
    Murrell, J. N., Shaw, G.: J. Chem. Phys. **46,** 1768 (1967)
21. Williams, D. R., Schaad, L. J., Murrell, J. N.: J. Chem. Phys. **47,** 4916 (1967)
22. Musso, G. F., Magnasco, V., Giardina, M. P.: J. Chem. Phys. **60,** 3749 (1974)
23. Löwdin, P.-O.: Advanc. Phys. **5,** 1 (1956) and Refs. therein
24. Clementi, E.: IBM J. Res. Develop. **9,** 2 (1969)
25. Leś, A.: Ph.D. Thesis, Warsaw 1975
26. O'Shea, S. F., Meath, W. J.: Mol. Phys. **28,** 1431 (1974)
27. Szalewicz, K., Jeziorski, B.: Mol. Phys. **38,** 191 (1979).
28. Bruch, L. W., Novaro, O., Flores, A.: J. Chem. Phys. **67,** 2371 (1977)