NON-ADDITIVE EFFECTS IN THE FIRST-ORDER INTERACTION ENERGY OF HYDROGEN MOLECULES*

By A. Leś and E. Radzio

Quantum Chemistry Laboratory, Institute of Basic Problems of Chemistry, University of Warsaw**

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The first-order three-body contribution to the interaction energy of three hydrogen molecules in the ground state has been examined. This energy is shown to be small for intermolecular distances close to the van der Waals minimum. It is also shown to be almost equal, but of opposite sign, to the Axilrod-Teller potential. The influence of the non-additive term on the cohesive energy of the o-H_2 crystal is also discussed.

1. Introduction

Recently, the interaction energy between hydrogen molecules has attracted considerable attention and has become a subject of theoretical [1] and experimental [2] investigations. Most of these investigations have concerned the short-range, repulsive part of the interaction potential. In this region, the interaction energy cannot be regarded as a sum of pair interactions and should contain the non-additive corrections. The recent ab initio calculations [3] suggest that the nonadditive term can be sufficiently well approximated by the three-body interactions when the distances between molecules exceed 3.5 a.u. At shorter intermolecular distances, the fourth and higher-order effects should be taken into account. However, if distances between molecules are about twice as large, i.e. 6 a.u., or more the non-additive effect should be relatively less important than the two-body interaction energy.

The purpose of the present work is to estimate the non-additivity of the first-order interaction energy between three hydrogen molecules at the distances corresponding to a van der Waals minimum of approximately 6.5 a.u. The non-additive contribution to the cohesive energy[1] of the o-H_2 crystal has also been calculated.

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** Address: Instytut Podstawowych Problemów Chemii UW, Pasteura 1, 02-093 Warszawa, Poland.
[1] excluding the zero-point energy.

2. Method

In the perturbation theory the interaction energy between N molecules is expressed as the sum of the first-order (electrostatic and exchange), the second-order (induction, dispersion and exchange) and the remaining higher-order interactions. Electrostatic and second-order dispersion interactions are known to be additive. Non-additive contributions resulting from induction and second-order exchange interactions are estimated to be small. In the case of three hydrogen atoms they are considerably smaller than the contributions from the first-order exchange interactions [4]. The calculations carried out for this system indicate that, for short internuclear distances, the non-additivity of the interaction energy is mainly due to the first-order exchange interactions and at larger distances — those exceeding the van der Waals minimum — it is well represented by the Axilrod–Teller potential [4, 5].

In the present work the non-additivity of the interaction energy is approximated by the sum of the first-order exchange contribution and the Axilrod–Teller potential. Unfortunately, we are not able to estimate the second-order non-additivity. However, previous results for the H_3 system [4] suggest that, at distances exceeding the van der Waals minimum, the second-order non-additivity is smaller that the first-order non-additivity and has the opposite sign.

According to the exchange perturbation theory the first-order interaction energy for a system of N molecules can be expressed as follows [8]:

$$E_{\text{int}}^{(1)} = \frac{\langle \Phi_0 | \mathscr{A} \sum_{A<B}^{N} V_{AB} | \Phi_0 \rangle}{\langle \Phi_0 | \mathscr{A} | \Phi_0 \rangle}, \tag{1}$$

where

$$\Phi_0 = \prod_{A}^{N} \psi_A, \qquad A, B = 1, 2, \ldots, N$$

is the simple product of the antisymmetrized wave functions describing isolated molecules, V_{AB} is the interaction operator between molecules A and B and $\mathscr{A}$ denotes the idempotent antisymmetrizer for all electrons in the system. According to Jeziorski et al. [8] Eq. (1) can be expanded as:

$$E_{\text{int}}^{(1)} = \sum_{A<B}^{N} W_{AB} + \sum_{A \neq B}^{N} 2 \sum_{p \in A} \sum_{r} D_{rp} \langle p | U_B | r \rangle$$

$$+ \sum_{A<B}^{N} 4 \sum_{p \in A} \sum_{q \in B} \sum_{r} \sum_{s} D_{rp} D_{sq} \left[\langle pr | \frac{1}{r_{12}} | qs \rangle - \tfrac{1}{2} \langle ps | \frac{1}{r_{12}} | qr \rangle \right], \tag{2}$$

where W_{AB} denotes the nuclear repulsion energy of the molecules A and B, the indices p and q are taken over all orbitals belonging to the molecules A and B respectively, r and s run over all molecular orbitals of the entire system and U_B is the electrostatic potential

of the nuclei in the molecule B. D_{rp} is an element of the matrix $\boldsymbol{D} = (1+\boldsymbol{S})^{-1}$ where $\boldsymbol{S}$ is the matrix of intermolecular overlap integrals.

In our calculation, Eq. (2) has been decomposed into a sum of two terms corresponding to two- and three-body interaction energies [8], e.g.

$$E_{\text{int}}^{(1)} = E^{(1)}(2,3)+E^{(1)}(3,3), \tag{3}$$

where $E^{(1)}(2, 3)$ denotes the two-body interaction energy between three hydrogen molecules and $E^{(1)}(3, 3)$ the three-body non-additive contribution to be investigated.

3. Results

The molecular orbital for the arbitrary H_2 molecule used in the present investigation has been allowed to take the form of various Gaussian expansions obtained by least-squares fits [9] to the Hartree–Fock orbital calculated by Kołos and Roothaan [10]. Five function bases have been employed in our calculations: (1|1), (2|0), (4|1), (5|2) and (7|3) where, generally, $(k|l)$ denotes a basis set composed of k 1s-type Gaussian functions centered at the nucleus of each hydrogen atom and l 1s-type Gaussians functions centered at the molecular center of mass.

TABLE I

Two-body energies for the system of $2H_2$ from the first-order perturbation theory [a]

Basis / R	(1|1)	(2|0)	(4|1)	(5|2)	(7|3)	B_3 [b]	B II [c]
4.0 [d]	1.1429×10^{-2}	0.7967×10^{-2}	0.8274×10^{-2}	0.8316×10^{-2}	0.8639×10^{-2}	0.9120×10^{-2}	1.0081×10^{-2}
6.5	0.1863×10^{-3}	0.0925×10^{-3}	0.1279×10^{-3}	0.1291×10^{-3}	0.1335×10^{-3}	0.1034×10^{-3}	0.1289×10^{-3}
10.0	0.3114×10^{-5}	0.2079×10^{-5}	0.3869×10^{-5}	0.3996×10^{-5}	0.4700×10^{-5}	0.5000×10^{-5}	0.3500×10^{-5}

[a] Axes of hydrogen molecules are parallel to one another and perpendicular to the line joining the molecular centers of mass. In all calculations the H–H bond lengths are fixed at 1.4 a.u. [b] Basis B_3: 4(1s), 3(2p) [11]. [c] Basis B II: 10(1s) [11]. [d] All quantities and results are expressed in atomic units, 1 a.u. of energy $= 4.3594\times10^{18}$ J.

In Table I the first-order interaction energies of two hydrogen molecules, calculated using the above five bases, are compared with the previous results for this system obtained also from a perturbative procedure [11].

It is seen that the results for the first-order two-body interaction energy obtained in the present work are close to the quoted values. In our opinion the differences are due to the different zeroth-order wave functions used by Kochanski and by ourselves. Moreover, one can see that the first-order interaction energy of two hydrogen molecules is rather insensitive to the quality of the molecular orbital employed in the calculations. Supposing that this conslusion holds in the case of three-body interactions, we have calculated most of the two- and three-body interaction energies by using bases denoted as (4|1) and (5|2). It is worth noting that the orbitals denoted as (1|1) and (2|0), in spite of being very crude approximations to the Hartree-Fock orbital, reproduce quite reasonably the two-body interaction energy.

TABLE II

Two- and three-body interaction energies for the system of 3 H_2 in various orders of perturbation theory [a]

R	$E^{(1)}(2,3)$	$E^{(2)}(2,3)$ [b]	$E^{(1)}(3,3)$	$E^{(3)}(3,3)$ [c]	$\varepsilon_3^{(1)}$ [d]			ε_3 [f]
					(4|1)	(2|0)	(1|1)	
4.0	24.82×10^{-3} (4.42×10^{-3}) [g]		-2.78×10^{-3} (-0.19×10^{-3}) [g]		−11.2 (12.4) [e]	−9.8 (11.2) [e]	−11.1 (13.2) [e]	
5.0	45.99×10^{-4} (3.97×10^{-4})		-2.64×10^{-4} (-0.64×10^{-5})		−5.7 (5.6)	−5.3 (5.4)	−6.5 (6.8)	
6.0	87.37×10^{-5} (2.85×10^{-5})		-2.24×10^{-5} (-0.02×10^{-5})		−2.6 (2.4)	−2.6 (2.3)	−3.4 (3.2)	
6.5	38.37×10^{-5}	-45.08×10^{-5}	-0.62×10^{-5}	0.32×10^{-5}	−1.6 (1.6)	−1.7 (1.5)	−2.4 (2.1)	4.5
7.0	17.47×10^{-5}	-28.90×10^{-5}	-0.16×10^{-5} $(-.053\times10^{-8})$	0.16×10^{-5}	−0.9 (1.0)	−1.0 (0.9)	−1.6 (1.4)	0.0
7.5	85.83×10^{-6}	-191.03×10^{-6}	-0.42×10^{-6}	0.88×10^{-6}	−0.5 (0.6)	−0.5 (0.6)	−1.0 (0.9)	−0.4

[a] Axes of the H_2 molecules are parallel to one another and perpendicular to the plane of the equilateral triangle formed by the molecular centers of mass, R being the separation of the centers. $E^{(1)}(2,3)$ and $E^{(1)}(3,3)$ are calculated using the (4|1) basis. [b] $E^{(2)}(2,3)$ is the dispersion energy estimated according to the formula given by Victor and Dalgarno [16]. [c] $E^{(3)}(3,3)$ has been approximated using the Axilrod-Teller formula [6, 7] with $C_9 = 48.9$ a.u. [17]. At distances less than the van der Waals minimum such an approximation is not valid. [d] $\varepsilon_3^{(1)} = \{E^{(1)}(3,3)/E^{(1)}(2,3)\} \times 100\%$. This quantity has been calculated using three basis sets (9, 4 and 3 simple Gaussians, respectively, per one molecule). [e] In columns 6, 7 and 8 the numbers in parentheses represent the values of the intermolecular overlap integral (between two hydrogen molecules). Each value is multiplied by 100. [f] $\varepsilon_3 = \{E^{(1)}(3,3)+E^{(3)}(3,3)\}/\{E^{(1)}(2,3)+E^{(2)}(2,3)\}\times100\%$. [g] In columns 2 and 4 the numbers in parentheses represent the respective first-order interaction energies for 3 helium atoms [8, 9].

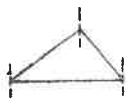
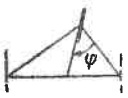
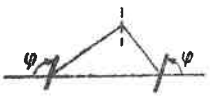
Two- and three-body interaction energies in various orders of the perturbation theory for three hydrogen molecules forming an equilateral triangle are listed in Table II. For comparison, the respective values for the isoelectronic system of three helium atoms are also given (in parentheses).

It is seen that the first-order three-body interaction energy $E^{(1)}$ (3,3) is smaller than $E^{(1)}(2, 3)$ by at least an order of magnitude and at large intermolecular distances decreases considerably faster than the two-body interaction energy (see the change of $\varepsilon_3^{(1)}$). It is necessary to pay attention to the fact that both of these energies decrease exponentially when the intermolecular distances increase.

The comparison of $E^{(1)}$ (3,3) for the isoelectronic systems of three hydrogen mloecules and of three helium atoms shows that in the atomic system the three-body contribution is considerably smaller than in the molecular system. This result is not surprising because the electronic clouds of the atoms are more concentrated around the nuclei.

TABLE III

Dependence of first-order two- and three-body interaction energies on the mutual rotations of three hydrogen molecules [a]

Geometry [b]	$E^{(1)}(2,3)$ [c]	$E^{(1)}(3,3)$	$\varepsilon_3^{(1)}$
	3.837×10^{-4}	-6.16×10^{-6}	-1.6
 $\varphi=30°$	3.227×10^{-4}	-6.94×10^{-6}	-2.2
 $\varphi=90°$	3.227×10^{-4}	-8.30×10^{-6}	-2.6
 $\varphi_1=60°$ $\varphi_2=30°$	4.871×10^{-4}	-10.24×10^{-6}	-2.1
 $\varphi=30°$	7.409×10^{-4}	-5.89×10^{-6}	-0.8

[a] The molecular centers of mass form an equilateral triangle measuring $R = 6.5$ a. u. on each side. [b] The broken lines denote that the axis of the molecule is perpendicular to the plane of the triangle; the solid lines denote that the axis of the molecule lies in the plane of the triangle. [c] The calculations of the first-order energies have been carried out using the (4|1) basis.

The dependence of $E^{(1)}(2,3)$, $E^{(1)}(3,3)$ and $\varepsilon_3^{(1)}$ on the mutual rotations of three hydrogen molecules is shown in Table III.

Figure 1 illustrates the changes in $\varepsilon_3^{(1)}$ resulting from changing angle in the triangle formed by the molecular centers of mass[2]. The same curve shape been obtained in the

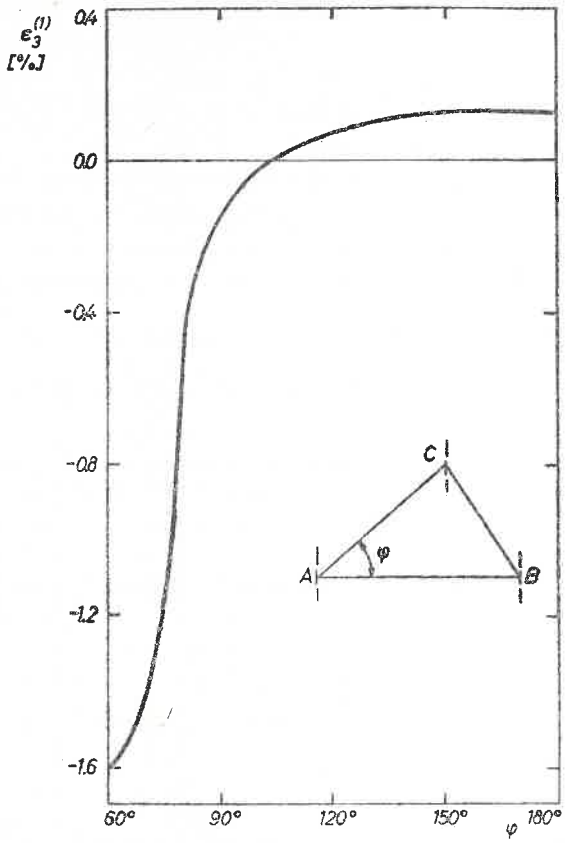


Fig. 1. Relative values of the first-order three-body interaction energy $\varepsilon_3^{(1)} = E^{(1)}(3,3)/E^{(1)}(2,3)$ for isosceles triangles formed by three hydrogen molecules. $R_{AB} = R_{AC} = 6.5$ a.u.

SCF calculations of the energy of the 3 H_2 system at shorter distances [3]. It may also be mentioned that similar curve shapes have been obtained for the first-order three-body effects in several rare gases [12, 13].

4. *Discussion*

Several conclusions follow from the above results. First we see that at distances corresponding to the van der Waals minimum, the non-additive three-body contribution $E^{(1)}(3,3)$ is small and represents only about 2% of the two-body first-order energy $E^{(1)}(2,3)$.

[2] The calculations for these configurations have been performed using the basis (5|2).

Moreover, $E^{(1)}(3,3)$ and the third-order three-body potential $E^{(3)}(3,3)$ have opposite signs but almost the same absolute values.

Near the van der Waals minimum, $E^{(1)}(3,3)$ and $E^{(1)}(2,3)$ depend on the mutual rotations of three hydrogen molecules. However, the relative three-body contribution to the additive two-body energy e. g. $\varepsilon_3^{(1)}$ does not strongly depend on the rotations being a function of the shape of the triangle formed by the molecular centers of mass (see Fig. 1). It is interesting to note that the $\varepsilon_3^{(1)}$ values can be easily estimated using very crude orbitals like (1|1) and (2|0). Moreover, if we expand the $E^{(1)}(3,3)$ and $E^{(1)}(2,3)$ terms as a power series of the intermolecular overlap integral S (up to an order of S^3) and if we use the Mulliken approximation to the multicenter integrals we obtain the following result holding for equilateral triangles:

$$\varepsilon_3^{(1)} \approx -S.$$

Hence, if a very crude orbital reproduces the correct values of the overlap integral, it may reproduce the relative three-body first-order energy as well. As Table II shows the (1|1) and (2|0) orbitals do it. The small values of the three-body potentials resulting from the first- and third-order of the perturbation theory and also their mutual cancellation suggest that the non-additivity of the interaction energy of three hydrogen molecules can be neglected at distances corresponding to the van der Waals minimum. Both non-additive corrections have also been estimated to the cohesive energy of the o–H_2 crystal. In the calculations of the first-order term the triples formed by the nearest neighbour-molecules have been included. In the case of the third-order term, the summation over the lattice has been performed by means of Axilrod's method [7].

In order to estimate the two-body contribution to the cohesive energy[3], we used the spherical symmetric potential recently obtained by fitting the integral cross section measurements [1]. This fit is a flexible multiparameter Morse-Spline-van der Waals (MSV) potential including long range dispersion constants C_6 calculated by Starkschall and Gordon [19] and C_8 by Margenau [20]. The summation over the fcc lattice has been performed by a method described elsewhere [18]. Assuming the nearest neighbour distance as $R_{NNS} = 7.1$ a. u. [15] we obtained for the two-body contribution to the cohesive energy the value -439.2 cal/mole. For the first-order non-additive contribution we obtained -8.0 cal/mole, whereas the Axilrod-Teller potential, representing here the third-order term, gives the value $+12.8$ cal/mole. Hence the whole non-additive contribution amounts to $+4.8$ cal/mole, and lowers the additive cohesive energy by about 1%. Thus, it seems that the non-additive effects are of little importance for estimating the cohesive energy. However, if the Axilrod-Teller potential is included in the calculation of solid state properties, the first-order term should not be neglected.

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[3] The o–H_2 crysal of the fcc-type lattice, space group $Pa\,3$, lattice constant is $a_0 = 10.04$ a. u., the nearest-neighbour distance is $R_0 = 7.1$ a. u. [15].

REFERENCES

[1] A. K. McMahan, M. Beck, J. A. Krumhansi, *Phys. Rev.* **A9**, 1852 (1974).
[2] R. Gegenbach, Ch. Hahn, W. Schrader, J. P. Toennies, *Theor. Chim. Acta* **34**, 199 (1974) and references therein.
[3] F. M. Ree, Ch. F. Bender, *Phys. Rev. Lett.* **32**, 85 (1974).
[4] B. Jeziorski, Thesis, University of Warsaw (1974).
[5] W. Kołos, in *The World of Quantum Chemistry*, D. Reidel Publishing Company, 1974, p. 31.
[6] B. M. Axilrod, *J. Chem. Phys.* **19**, 724 (1951); B. M. Axilrod, E. Teller, *J. Chem. Phys.* **11**, 299 (1943).
[7] B. M. Axilrod, *J. Chem. Phys.* **17**, 1349 (1949); **19**, 719 (1951).
[8] B. Jeziorski, M. Bulski, L. Piela, *Int. J. Quantum Chem.* **10**, 281 (1976).
[9] A. Leś, unpublished results.
[10] W. Kołos, C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 219 (1960).
[11] E. Kochanowski, *J. Chem. Phys.* **58**, 5823 (1973).
[12] L. Jansen, *Adv. Quantum Chem.* **2**, 119 (1965).
[13] O. A. Novaro, V. Beltran-Lopez, *J. Chem. Phys.* **56**, 815 (1972).
[14] J. C. Reich, R. D. Etters, *J. Low Temp. Phys.* **6**, 229 (1972).
[15] H. M. James, J. C. Reich, *Phys. Rev.* **162**, 649 (1967).
[16] G. A. Victor, A. Dalgarno, *J. Chem. Phys.* **53**, 1316 (1970).
[17] P. W. Langhoff, M. Karplus, *J. Chem. Phys.* **53**, 233 (1970).
[18] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York 1954.
[19] G. Starkshall, R. G. Gordon, *J. Chem. Phys.* **54**, 663 (1971).
[20] A. A. Evett, H. Margenau, *Phys. Rev.* **90**, 1021 (1953); A. A. Evett, H. Margenau, *J. Chem. Phys.* **21**, 958 (1953).