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Accurate coefficient of the Axilrod-Teller triple-dipole term for three hydrogen atoms

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Using the very accurate first order perturbation wave function reported recently for the van der Waals interaction between two ground-state hydrogen atoms, we derive an accurate coefficient of the Axilrod-Teller triple-dipole term for three ground-state hydrogen atoms, which is an important leading term of the nonadditive three-body long-range force.

I. INTRODUCTION

In a very recent paper,¹ we have shown that perturbation equations for the H(1s)-H(1s) van der Waals interaction can be exactly solved in their Schrödinger forms by using the momentum-space technique. The first order equation (with respect to the perturbation potential) has been actually solved and the leading term of the first order perturbation wave function proportional to R^{-3} has been rigorously obtained where R is the internuclear distance.

In the present paper, we show that after simple modification the above first order function of the two hydrogen atomic system can be used to evaluate an accurate coefficient of the leading term of nonadditive long-range forces, which is often referred to as the Axilrod-Teller triple-dipole term, among three ground-state hydrogen atoms. It is well known that the total interaction energy of more than two atoms is not equal to the sum of pairwise interaction energies and that the nonadditive contribution for the interaction is frequently significant (see e.g., Refs. 2-7 for review). The Axilrod-Teller energy is the leading term of this nonadditive contribution, but its coefficient ν has not been calculated, to our knowledge, so accurately as the dispersion coefficient C_6 , probably because the former requires the third order perturbation theory as compared with the second order theory for the latter. In the following, we shall show that ν can be straightforwardly expressed in terms of the coefficients $b_{nn'}$, given in Ref. 1 and report an accurate numerical value of ν .

II. AXILROD-TELLER ENERGY

A. First order perturbation wave function for two hydrogen atoms

Here we briefly outline the property of the first order function of the H(1s)-H(1s) long-range interaction for the later convenience. The leading term $\psi_3(1,2)$ obtained in Ref. 1 can be rewritten as

$$\psi_3(1,2) = R^{-3} \chi(1,2), \quad (1a)$$

$$\chi(i,j) = \sum_{n,n'=2}^{\infty} b_{nn'} \{ np_{+1}(i)n'p_{-1}(j) + np_{-1}(i)n'p_{+1}(j) + 2[np_0(i)n'p_0(j)] \}, \quad (1b)$$

where np_m denotes the normalized hydrogenic orbital with the quantum numbers $(n,1,m)$ and the common exponent unity. The z axis is taken along the internuclear vector. The expansion coefficients $b_{nn'}$ ($=b_{n'n}$) are exactly determined by a set of inhomogeneous linear equations¹

$$\begin{aligned} (1-n^{-1})[a_{-}(n'+1,1)b_{nn'+1} + b_{nn'} + a_{+}(n'-1,1)b_{nn'-1}] \\ + (1-n'^{-1})[a_{-}(n+1,1)b_{n+1n'} + b_{nn'} + a_{+}(n-1,1)b_{n-1n'}] \\ = \delta_{n2}\delta_{n'2} + (1/\sqrt{6})(\delta_{n2}\delta_{n'3} + \delta_{n3}\delta_{n'2}) + (1/6)\delta_{n3}\delta_{n'3}, \\ n, n' = 2, 3, 4, \dots, \end{aligned} \quad (2a)$$

where δ_{ij} represents Kronecker's delta and

$$a_{-}(n,l) = (1/2)[(n+l)(n-l-1)/n(n-1)]^{1/2}, \quad (2b)$$

$$a_{+}(n,l) = (1/2)[(n-l)(n+l+1)/n(n+1)]^{1/2}. \quad (2c)$$

Because of the normalization constant of the function np_m , the present $b_{nn'}$ differ by factor 32 from those of Ref. 1. Since Eq. (2a) is a set of equations for infinite number of unknown $b_{nn'}$, it is solved in practice after the truncation at some $n, n_{\max}$, which is so chosen as to achieve the required accuracy. When the leading term of the first order wave function [Eq. (1)] has been used, an extremely accurate value of

$$C_6 = -6.499\,026\,705\,405\,83 \quad (\text{for } n_{\max} = 20) \quad (3)$$

has been found for the dispersion coefficient proportional to R^{-6} in a surprisingly simple manner.¹

B. Axilrod-Teller triple-dipole term for three hydrogen atoms

The nonadditive long-range force first arises from the third order perturbation energy $E^{(3)}$ which can be written in the present case as (see, e.g., Ref. 8)

$$E^{(3)} = \langle \Psi^{(1)}(1,2,3) | V^{(1)}(1,2,3) | \Psi^{(1)}(1,2,3) \rangle, \quad (4)$$

since $E^{(1)} = 0$ and $\langle \Psi^{(1)} | \Psi^{(0)} \rangle = 0$, in which $\Psi^{(0)} = 1s(1)1s(2)1s(3)$ and $\Psi^{(1)}$ are the zeroth and first order wave functions, respectively. $V^{(1)}$ is the perturbation potential which includes all the interatomic Coulomb interactions.

The Axilrod-Teller energy is the leading term of Eq. (4), for which $V^{(1)}$ is approximated by its dipole parts^{2-7,9-13}

FIG. 1. Local coordinate systems for three hydrogen atoms. For each pair of atoms i and j , the z axis is taken along the internuclear vector $\mathbf{R}_{ij}$ and the x and y axes are, respectively, normal to and in the plane of the three atoms.

$$V^{(1)}(1,2,3) = V_3(1,2) + V_3(2,3) + V_3(3,1), \quad (5a)$$

where

$$V_3(i,j) = R_{ij}^{-3} W(i,j), \quad (5b)$$

$$W(i,j) = x_i x_j + y_i y_j - 2z_i z_j. \quad (5c)$$

Note that each $V_3(i,j)$ is described by the "local" Cartesian coordinates (Fig. 1) with its z axis along the internuclear vector $\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i$. R_{ij} means $|\mathbf{R}_{ij}|$ and $\mathbf{r}_i = (x_i, y_i, z_i)$ is the position of the i th electron measured from the nuclear position $\mathbf{R}_i$. Since each atom has only one electron and there is no electron exchange between atoms, we use the same label 1,2,3 or i,j for an electron and its partner nucleus.

Following the discussion given in Refs. 14 and 15, the leading term of $\Psi^{(1)}$ can be expressed as

$$\Psi^{(1)}(1,2,3) = 1s(1)\psi_3(2,3) + 1s(2)\psi_3(3,1) + 1s(3)\psi_3(1,2), \quad (6a)$$

where

$$\psi_3(i,j) = R_{ij}^{-3} \chi(i,j). \quad (6b)$$

The function $\chi(i,j)$ is defined in Eq. (1b), but it is convenient to use its Cartesian representation

$$\begin{aligned} \chi(3,1) = & - \sum_{n,n'=2}^{\infty} b_{nn'} \{ np_x(3)n'p_x(1) + (\cos^2 \theta_1 - 2 \sin^2 \theta_1) np_y(3)n'p_y(1) \\ & - 3 \cos \theta_1 \sin \theta_1 [np_z(3)n'p_y(1) + np_y(3)n'p_z(1)] + (\sin^2 \theta_1 - 2 \cos^2 \theta_1) np_z(3)n'p_z(1) \}, \end{aligned} \quad (9a)$$

$$\begin{aligned} \chi(2,3) = & - \sum_{n,n'=2}^{\infty} b_{nn'} \{ np_x(2)n'p_x(3) + (\cos^2 \theta_2 - 2 \sin^2 \theta_2) np_y(2)n'p_y(3) \\ & + 3 \cos \theta_2 \sin \theta_2 [np_z(2)n'p_y(3) + np_y(2)n'p_z(3)] + (\sin^2 \theta_2 - 2 \cos^2 \theta_2) np_z(2)n'p_z(3) \}, \end{aligned} \quad (9b)$$

in the unified coordinates defined by the internuclear vector $\mathbf{R}_{12}$. Inserting Eqs. (5c), (9a), and (9b) into Eq. (7c), we obtain

$$E^{(3)} = 6(R_{12}R_{23}R_{31})^{-3} [I_x + I_y - 2I_z], \quad (10)$$

where

$$\begin{aligned} I_x = & \langle 1s(2)\chi(3,1) | x_1 x_2 | 1s(1)\chi(2,3) \rangle \\ = & \sum_{n,n'} \sum_{m,m'} b_{nn'} b_{mm'} \langle n'p_x(1) | x_1 | 1s(1) \rangle \langle 1s(2) | x_2 | mp_x(2) \rangle \langle np_x(3) | m'p_x(3) \rangle \\ = & \sum_{n,n'} \sum_{m,m'} b_{nn'} b_{mm'} I_n I_m J_{nm'}, \end{aligned} \quad (11a)$$

$$\begin{aligned} \chi(i,j) = & - \sum_{n,n'=2}^{\infty} b_{nn'} \{ n\bar{p}_x(i)n'\bar{p}_x(j) \\ & + n\bar{p}_y(i)n'\bar{p}_y(j) - 2[n\bar{p}_z(i)n'\bar{p}_z(j)] \}, \end{aligned} \quad (6c)$$

where bars are used to emphasize that the local coordinate system is also employed here as in $W(i,j)$.

Substituting Eqs. (5a) and (6a) into Eq. (4), we have

$$\begin{aligned} E^{(3)} = & 2 \langle 1s(2)\psi_3(3,1) | V_3(1,2) | 1s(1)\psi_3(2,3) \rangle \\ & + 2 \langle 1s(3)\psi_3(1,2) | V_3(2,3) | 1s(2)\psi_3(3,1) \rangle \\ & + 2 \langle 1s(1)\psi_3(2,3) | V_3(3,1) | 1s(3)\psi_3(1,2) \rangle, \end{aligned} \quad (7a)$$

since all the remaining 21 integrals vanish due to the odd symmetry of integrands. Using Eqs. (5b) and (6b), Eq. (7a) is simplified as

$$\begin{aligned} E^{(3)} = & 2(R_{12}R_{23}R_{31})^{-3} [\langle 1s(2)\chi(3,1) | W(1,2) | 1s(1)\chi(2,3) \rangle \\ & + \langle 1s(3)\chi(1,2) | W(2,3) | 1s(2)\chi(3,1) \rangle \\ & + \langle 1s(1)\chi(2,3) | W(3,1) | 1s(3)\chi(1,2) \rangle] \\ = & 6(R_{12}R_{23}R_{31})^{-3} \langle 1s(2)\chi(3,1) | W(1,2) | 1s(1)\chi(2,3) \rangle, \end{aligned} \quad (7b)$$

where we have used the fact that the three integrals in the square brackets of Eq. (7b) are equivalent.

In order to perform the integration of Eq. (7c), we must now unify the three local coordinate systems appearing in the integral. To do this, we transform $\chi(3,1)$ and $\chi(2,3)$ functions into the $\mathbf{R}_{12}$ coordinates used for $W(1,2)$. From the geometrical consideration (cf. Fig. 1), we see the transformations are

$$\begin{pmatrix} \bar{p}_x \\ \bar{p}_y \\ \bar{p}_z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\cos \theta_1 & +\sin \theta_1 \\ 0 & -\sin \theta_1 & -\cos \theta_1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \quad (8a)$$

for $\bar{p}$ functions in $\chi(3,1)$ and

$$\begin{pmatrix} \bar{p}_x \\ \bar{p}_y \\ \bar{p}_z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\cos \theta_2 & -\sin \theta_2 \\ 0 & +\sin \theta_2 & -\cos \theta_2 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \quad (8b)$$

for $\bar{p}$ functions in $\chi(2,3)$. We then have

$$\begin{aligned}
I_y &= \langle 1s(2)|\chi(3,1)|y_1y_2|1s(1)\chi(2,3)\rangle \\
&= \sum_{n,n'} \sum_{m,m'} b_{nn'} b_{mm'} [(\cos^2 \theta_1 - 2 \sin^2 \theta_1)(\cos^2 \theta_2 - 2 \sin^2 \theta_2) \langle n'p_y(1)|y_1|1s(1)\rangle \langle 1s(2)|y_2|mp_y(2)\rangle \langle np_y(3)|m'p_y(3)\rangle \\
&\quad - 9 \cos \theta_1 \sin \theta_1 \cos \theta_2 \sin \theta_2 \langle n'p_y(1)|y_1|1s(1)\rangle \langle 1s(2)|y_2|mp_y(2)\rangle \langle np_z(3)|m'p_z(3)\rangle] \\
&= [(\cos^2 \theta_1 - 2 \sin^2 \theta_1)(\cos^2 \theta_2 - 2 \sin^2 \theta_2) - 9 \cos \theta_1 \sin \theta_1 \cos \theta_2 \sin \theta_2] \sum_{n,n'} \sum_{m,m'} b_{nn'} b_{mm'} I_n I_m J_{nm}, \quad (11b)
\end{aligned}$$

$$\begin{aligned}
I_z &= \langle 1s(2)|\chi(3,1)|z_1z_2|1s(1)\chi(2,3)\rangle \\
&= \sum_{n,n'} \sum_{m,m'} b_{nn'} b_{mm'} [(\sin^2 \theta_1 - 2 \cos^2 \theta_1)(\sin^2 \theta_2 - 2 \cos^2 \theta_2) \langle n'p_z(1)|z_1|1s(1)\rangle \langle 1s(2)|z_2|mp_z(2)\rangle \langle np_z(3)|m'p_z(3)\rangle \\
&\quad - 9 \cos \theta_1 \sin \theta_1 \cos \theta_2 \sin \theta_2 \langle n'p_z(1)|z_1|1s(1)\rangle \langle 1s(2)|z_2|mp_y(2)\rangle \langle np_y(3)|m'p_y(3)\rangle] \\
&= [(\sin^2 \theta_1 - 2 \cos^2 \theta_1)(\sin^2 \theta_2 - 2 \cos^2 \theta_2) - 9 \cos \theta_1 \sin \theta_1 \cos \theta_2 \sin \theta_2] \sum_{n,n'} \sum_{m,m'} b_{nn'} b_{mm'} I_n I_m J_{nm}, \quad (11c)
\end{aligned}$$

in which

$$\begin{aligned}
I_n &= \langle 1s|x|np_x\rangle = \langle 1s|y|np_y\rangle = \langle 1s|z|np_z\rangle \\
&= \delta_{2n} + (1/\sqrt{6})\delta_{3n}, \quad (12a)
\end{aligned}$$

$$\begin{aligned}
J_{nm} &= \langle np_x|mp_x\rangle = \langle np_y|mp_y\rangle = \langle np_z|mp_z\rangle \\
&= a_-(n,1)\delta_{n,m+1} + \delta_{nm} + a_+(n,1)\delta_{n,m-1}. \quad (12b)
\end{aligned}$$

After simple manipulation of the angular parts, we finally obtain the desired result of the Axilrod-Teller triple-dipole term

$$E^{(3)} = \nu(R_{12}R_{23}R_{31})^{-3}(1 + 3 \cos \theta_1 \cos \theta_2 \cos \theta_3), \quad (13a)$$

where θ_3 is the third internal angle (see Fig. 1) and the coefficient ν is given by

$$\nu = 18 \sum_{n,n'} \sum_{m,m'} b_{nn'} b_{mm'} I_n I_m J_{nm}. \quad (13b)$$

Due to its fourfold summation, Eq. (13b) appears to be inconvenient at first sight, but we can understand from Eqs. (12a) and (12b) that the number of nonvanishing terms is rather limited. We have evaluated Eq. (13b) based on $b_{nn'}$ obtained from the solution of Eq. (2a) with the truncation at $n_{\max}$. The results are summarized in Table I. The convergence of ν with respect to $n_{\max}$ is rapid and the ν value from $n_{\max} = 20$ is trustworthy to within one unit in the last decimal place. This value is compared in Table II with those reported previously, which demonstrates that the present method gives an extremely accurate value in spite of its simplicity. An extension of the present technique to the higher order Axilrod-Teller terms is also hopeful. Finally, we note that the present ν value given in Table I can be expressed as a fractional number; for example,

$$\begin{aligned}
n_{\max} = 3; \quad \nu &= 67\,707/3136, \\
n_{\max} = 4; \quad \nu &= 80\,451\,323/3\,717\,184, \\
n_{\max} = 5; \quad \nu &= 2\,553\,334\,860\,709/117\,977\,502\,752.
\end{aligned}$$

TABLE I. Coefficient of the Axilrod-Teller triple-dipole term for three ground-state hydrogen atoms.

$n_{\max}$	ν
2	18.000 000 000 000 000
3	21.590 242 346 938 776
4	21.643 083 312 529 054
5	21.642 557 277 011 993
6	21.642 470 426 140 755
7	21.642 464 869 444 960
8	21.642 464 535 546 714
9	21.642 464 512 790 883
10	21.642 464 510 872 936
11	21.642 464 510 668 440
12	21.642 464 510 641 340
13	21.642 464 510 637 014
14	21.642 464 510 636 206
15	21.642 464 510 636 035
16	21.642 464 510 635 994
17	21.642 464 510 635 983
18	21.642 464 510 635 980
19	21.642 464 510 635 979
20	21.642 464 510 635 979

TABLE II. Comparison of several ν values for three ground-state hydrogen atoms.

Authors	ν
Midzuno-Kihara (Ref. 13)	21.4
Musher (Ref. 15)	23.1
Chan-Dalgarno (Ref. 16)	21.642 5
Bell (Ref. 17)	21.642 7
Bell-Kingston (Ref. 18)	21.645
Dalgarno-Victor (Ref. 19)	21.642
Present	21.642 464 510 635 979

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¹T. Koga and S. Matsumoto, J. Chem. Phys. **82**, 5127 (1985).

²A. Dalgarno and W. D. Davison, Adv. At. Mol. Phys. **2**, 1 (1966).

³A. Dalgarno, Adv. Chem. Phys. **12**, 143 (1967).

⁴H. Margenau and J. Stamper, Adv. Quantum Chem. **3**, 129 (1967).

⁵H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, 2nd ed. (Pergamon, Oxford, 1971).

⁶P. R. Certain and L. W. Bruch, *MTP International Review of Science. Physical Chemistry. Ser. 1. Vol. 1. Theoretical Chemistry*, edited by W.

Byers Brown (Butterworths, London, 1972), pp. 113-165.

⁷G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces: Their Origin and Determination* (Clarendon, Oxford, 1981).

⁸J. O. Hirschfelder, W. Byers Brown, and S.T. Epstein, Adv. Quantum Chem. **1**, 256 (1964).

⁹B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

¹⁰Y. Muto, Proc. Phys. Math. Soc. Jpn. **17**, 629 (1943).

¹¹B. M. Axilrod, J. Chem. Phys. **17**, 1349 (1949).

¹²B. M. Axilrod, J. Chem. Phys. **19**, 719 (1951).

¹³Y. Midzuno and T. Kihara, J. Phys. Soc. Jpn. **11**, 1045 (1956).

¹⁴N. R. Kestner and O. Sinanoglu, J. Chem. Phys. **38**, 1730 (1963).

¹⁵J. I. Musher, J. Chem. Phys. **39**, 2409 (1963).

¹⁶Y. M. Chan and A. Dalgarno, Mol. Phys. **9**, 525 (1965).

¹⁷R. J. Bell, Proc. Phys. Soc. **86**, 519 (1965).

¹⁸R. J. Bell and A. E. Kingston, Proc. Phys. Soc. **88**, 901 (1966).

¹⁹A. Dalgarno and G. A. Victor, Mol. Phys. **10**, 333 (1966).