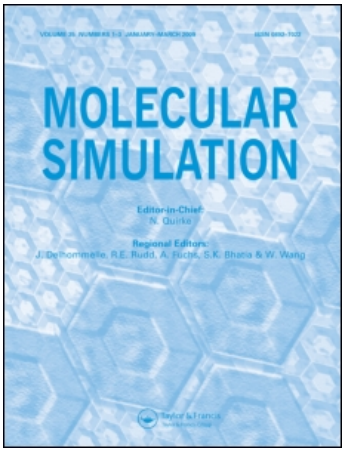

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The Spherical Expansion of H_2 Dimer Interaction Energy by Double Symmetry-Adapted Perturbation Theory

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THE SPHERICAL EXPANSION OF H_2 DIMER INTERACTION ENERGY BY DOUBLE SYMMETRY-ADAPTED PERTURBATION THEORY

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The weak interaction energy of H_2 dimer is studied by double symmetry-adapted perturbation theory (SAPT) within second-order of intermolecular and intramonomer perturbation for molecular simulations. The assumed orientations of H_2 dimer are linear, parallel, T type and X type. Among four orientations T orientation is the most stable, while linear orientation is the most repulsive. The second-order dispersion energy $E_{disp}^{(2)}$ is the most attractive contribution in all orientations. The interaction energy has the anisotropy, so we expressed our total interaction energy by the spherical expansion to compare with the experimental value. The isotropic interaction energy is about 85% of the experimental value.

KEY WORDS: Double symmetry-adapted perturbation theory, H_2 dimer, spherical expansion

I. INTRODUCTION

The theoretical study of intermolecular interaction is considerably important in Monte Carlo and molecular dynamics simulations. However, the calculation of accurate interaction energy is very difficult, even for the simplest molecular system, the H_2 dimer [1]. Because the interaction energy is of the order of 10^{-5} hartree and in such a nonpolar system the attractive contribution is almost determined by the dispersion energy.

The interaction energy of the H_2 dimer is calculated by various methods. Kochanski [2] calculated it as the sum of Hartree-Fock (HF) interaction energy by the supermolecule method and HF dispersion energy by the second-order perturbation theory. Burton *et al.* [3], [4] calculated it by the supermolecule method with coupled electron pair approximation 2. Chalasinski [5] has taken account of the intracorrelation correction to the first-order energy. Moreover, Lavendy *et al.* [6], [7] calculated it by the supermolecule method with configuration interaction. But these calculated energies range from 75 to 110 μhartree [1]-[7], while the experimental value is 110 ± 5.5 μhartree [8].

In the supermolecule method the interaction energy, obtained by subtracting the sum of the each monomer energy from the supermolecule energy [9], is much smaller than the supermolecule (or monomer) energy, and can not be divided into physically meaningful terms directly. While the symmetry-adapted perturbation theory (SAPT) [10]–[14] gives the interaction energy directly, and takes account of electron exchange effects between interacting molecules. The total energy is obtained as the sum of physically meaningful terms;

$$E_{tot} = E_{pol}^{(1)} + E_{ex}^{(1)} + E_{pol}^{(2)} + E_{ex}^{(2)} \ldots, \tag{1}$$

where the first-order $E_{pol}^{(1)}$ contributes to the classical Coulomb or electrostatic energy, and $E_{pol}^{(2)}$ is decomposed into the quantum mechanical dispersion (disp) $E_{disp}^{(2)}$ and the induction (ind) $E_{ind}^{(2)}$ energies;

$$E_{pol}^{(2)} = E_{disp}^{(2)} + E_{ind}^{(2)}. \tag{2}$$

$E_{ex}^{(2)}$ means the first-order exchange energy which originates from the electron exchange between interacting molecules, and the second-order exchange energy $E_{ex}^{(1)}$ is decomposed into the exchange-dispersion (exd) $E_{exd}^{(2)}$ and the exchange induction (exi) $E_{pol}^{(2)}$ energies.

To estimate decomposed energy terms, the exact or accurately correlated wave function should be known, but it is too complicated. Then HF wave function is used in general as the zeroth-order one. Starting from HF wave function, the electron correlation contribution in monomer (intracorrelation) is obtained by applying the double perturbation [15]. In this double symmetry-adapted perturbation theory [16]–[18], the interaction energy is expanded in a perturbation series of not only intermolecular potential but also intracorrelation Møller-Plesset fluctuation potential.

In a preceding paper [18] the formulas of intracorrelated energy terms within double SAPT are derived and the numerical result of H_2 dimer has been reported. For the molecular simulations, however, the analytical potential functions are required. So in this paper, the spherical expansion [19], [20] has been done for H_2 dimer, and the isotropic potential is obtained.

In Section II the method of calculations is described, and in Section III the results of numerial computations for H_2 dimer are presented. Finally, some conclusions are given in Section IV.

II METHOD OF CALCULATION

Let us consider the interaction of molecules A and B. The Schrödinger equation for this system is assumed as

$$(F + \lambda V + \mu W)\Psi = E\Psi, \tag{3}$$

where F is divided into F_A and F_B, which are HF Hamiltonians for monomers A and B. V is the intermolecular interaction perturbation operator and W is the sum of W_A and W_B, where W_A is the Møller-Plesset fluctuation perturbation operator to evaluate intracorrelation in monomer A, and λ, μ, are expansion parameters.

The total energy E of this system can be expanded as

$$E = \sum_{k=0}^{\infty} \lambda^k E^{(k)}, \tag{4}$$

$$= \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \lambda^k \mu^l E^{(kl)}, \tag{5}$$

where $E^{(kl)}$ is of the kth-order in V, the lth-order in W. The wave function Ψ is expanded consequently

$$\Psi = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \lambda^k \mu^l \psi^{(kl)}. \tag{6}$$

Inserting Equation (5) and Equation (6) into Equation (3) with Dalgarno interchange theorem [15], the explicit expressions can be obtained.

The energy terms are limited to the second-order of V and W, i.e., $k \leq 2$ and $l \leq 2$ in Equation (5) [18]. The total interaction energy E_{tot} is approximated as

$$E_{tot} = E_{pol}^{(1)} + E_{ex}^{(1)} + E_{disp}^{(2)} + E_{ind}^{(2)} + E_{exd}^{(2)} + E_{exi}^{(2)}, \tag{7}$$

where $E_{pol}^{(1)}$ is Coulomb, $E_{ex}^{(1)}$ first-order exchange, $E_{disp}^{(2)}$dispersion, $E_{ind}^{(2)}$ induction, $E_{exd}^{(2)}$ exchange-dispersion and $E_{exi}^{(2)}$ exchange-induction energy respectively.

III RESULTS OF NUMERICAL COMPUTATIONS

We have employed $(10s2p1d)/[4s2p1d]$ basis set for a H atom [18]. The s orbital for this basis set was composed by the (6; 2; 1; 1) contraction of Schmidt (10s) functions [21]. The polarization exponents were 0.20, 0.60 for p orbitals and 0.2 for d orbital, which were optimized by the maximum of the absolute value of dispersion energy. For the polarization function five d-type orbitals were used. All the decomposed interaction energies were calculated with the dimer-centered basis set. We have used the *Gaussian* 86 *ab initio* program package [22] for the calculation of the atomic integrals, orbital energies and coefficients.

We have computed intermolecular interaction energies for four different orientations of H_2 dimer. These are; parallel (P), linear (L), T type (T) and X type (X) orientations. In this study the nuclear distance of a hydrogen molecule is fixed at the experimental value (vibrationally averaged) 1.449*a.u.* [8]. The intermolecular distance R is defined as the distance between the center of mass of two molecules and R ranges from 5.0*a.u.* to 8.0*a.u.*.

We show the total interaction energies [18] of H_2 dimer for four orientations in Table I and Figure 1. The interaction potential is strongly anisotropic, and total interaction energies are attractive in all orientations. T orientation is the most attractive , then X, P orientations come and L orientation is the last. The van der Waals

Table 1 The total interaction energy E_{tot} for four orientations of H_2 dimer at various interatomic distance R. Energies in μhartree.

type	*5.0*	*6.0*	*6.5*	*7.0*	*7.5*	*8.0*
P	1074.10	40.52	−35.13	−45.71	−38.01	−27.83
L	2452.65	230.25	27.51	−27.25	−33.00	−25.69
T	1075.43	−105.40	−159.10	−141.19	−108.67	−79.40
X	971.15	1.28	−61.25	−63.71	−50.82	−37.19

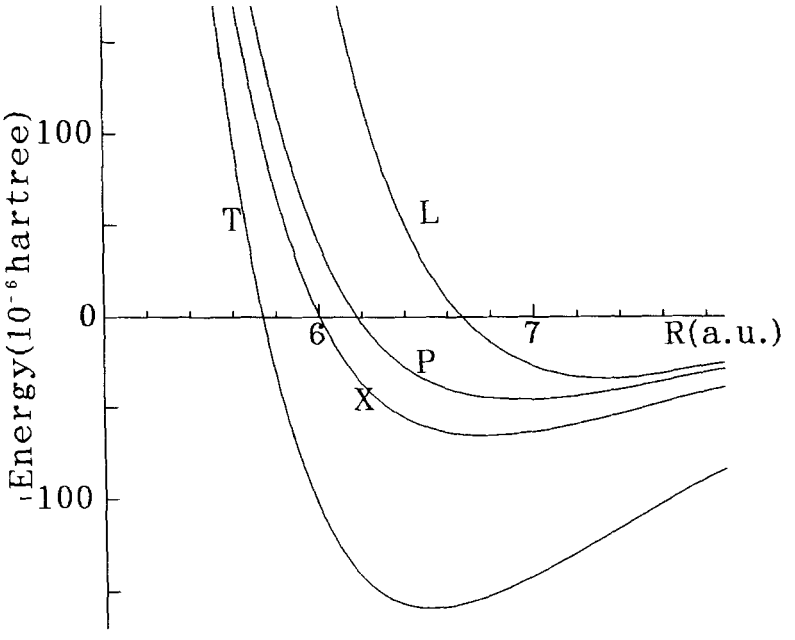

Figure 1 The total interaction energies E_{tot} for four orientations of H_2 dimer.

minimum in P, L, T and X orientations can be found about 7.0, 7.5, 6.5 and 7.0 a.u. respectively.

For the analytical potential functions, the spherical expansion [19] has been done at first. We expand our results in terms of the body-fixed coordinates to compare with the experimental value. The spherical expansion of interaction energy E is given as

$$E(\hat{R}, \hat{r}_1, \hat{r}_2) = \sum_{q_1 q_2 \mu} V_{q_1 q_2 \mu}(R)\, Y_{q_1 q_2 \mu}(\hat{r}_1, \hat{r}_2), \tag{8}$$

where

$$Y_{q_1 q_2 \mu}(\hat{r}_1, \hat{r}_2) = 4\pi \left(Y_{q_1 \mu}(\hat{r}_1) Y_{q_2 - \mu}(\hat{r}_2) + Y_{q_1 - \mu}(\hat{r}_1) Y_{q_2 \mu}(\hat{r}_2) \right) (1 + \delta_{\mu 0})^{-1}. \tag{9}$$

The function $Y_{q_1 \mu}(\hat{r})$ is a spherical harmonic, $\hat{R}$ is the intermolecular vector, and $\hat{r}_1$, $\hat{r}_2$ are the intramolecular unit vectors showing the directions of molecular axes. We limit ourselves to V_{000}, V_{200}, V_{220} and V_{222} terms in Equation (8). V_{000} means the isotropic potential and V_{200}, V_{220} and V_{222} the anisotropic potential.

In Figure 2 we show those terms of our calculation and experimental van der Waals minimum. Our interaction energy minimum is about -95 μhartree at R = 6.8 a.u. for the V_{000} term, while the experimental value is -110 ± 5.5 μhartree at R = 6.5 a.u. [8]. Thus we obtained more than 85% of the experimental value, but we suppose the possibility that the experimental value may include the three-body or many-body effects. Among the anisotropic terms V_{200} has a few minimum, V_{220} and V_{222} are both repulsive.

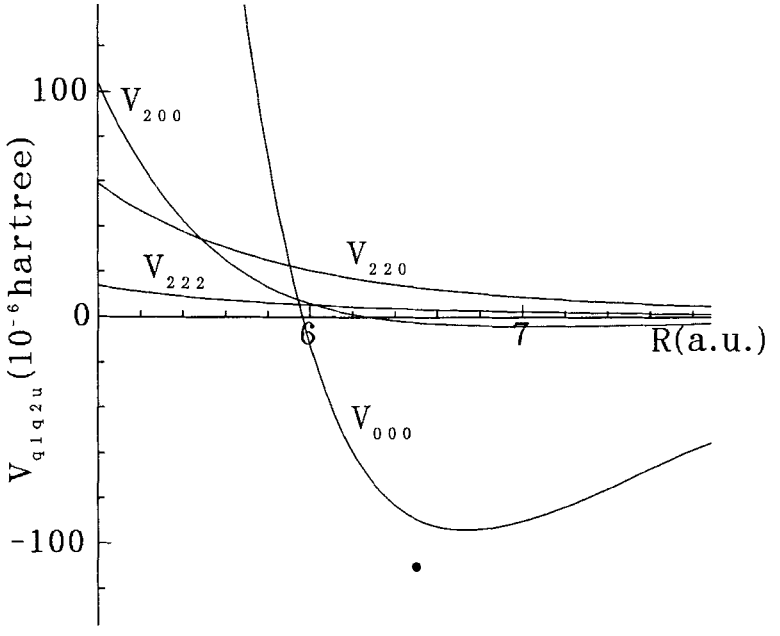

Figure 2 The spherical expansion of the total interaction energies E_{tot} of H_2 dimer. The dot is the experimental minimum value [8].

In Figure 3 the decomposed energy terms of V_{000} is shown. The dispersion energy $E^{(2)}_{disp}$ is the most attractive contribution, then the Coulomb energy $E^{(1)}_{pol}$ and the induction energy $E^{(2)}_{ind}$ come. The most repulsive contribution is the first-order exchange energy $E^{(1)}_{ex}$, then the second-order exchange-dispersion energy $E^{(2)}_{exd}$ and the second-order exchange-induction energy $E^{(2)}_{exi}$ come. We see the second-order exchange-induction energy $E^{(2)}_{exi}$ cancels most of the induction energy $E^{(2)}_{ind}$ particularly in smaller distance.

In Figure 4 we compare our result of V_{000} term with those by other authors [2], [5], [7]. Our result is a little more repulsive than others, especially at small distance, and our van der Waals minimum is a little larger than those by other authors, but the overall behavior is almost the same.

Finally the comparison of our V_{200} term with those by other authors [2], [5], [7] is shown in Figure 5. Our minimum of V_{200} is about -4.0 μhartree at R = 7.0 a.u. and a little larger than other results. Thus our V_{200} term is also more repulsive than other authors, particularly in smaller distance.

IV CONCLUSION

We have calculated the intermolecular interaction energies of H_2 dimers within the framework of the double SAPT. We have obtained about 85% of the experimental value which, we suppose, may include the three- or many-body effects. Further we

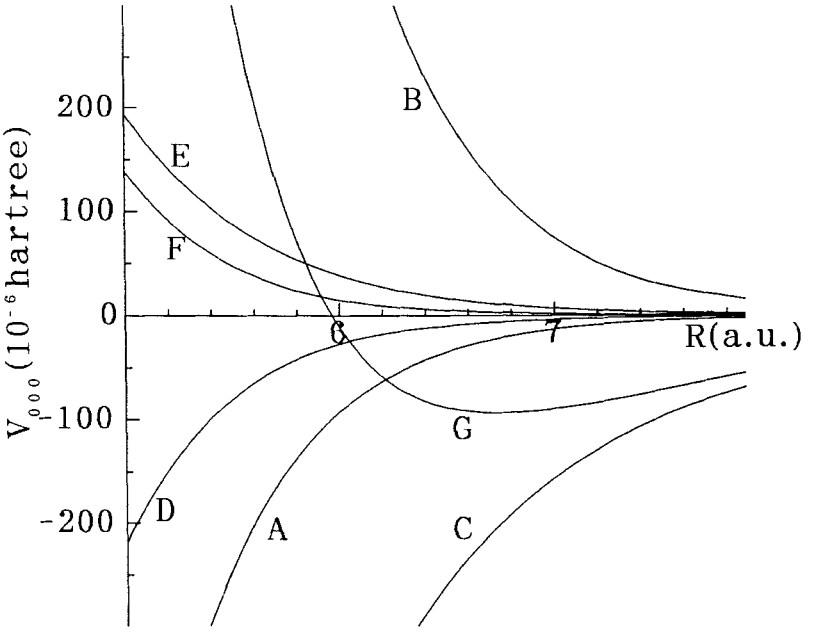

Figure 3 The decompositions of the isotropic term V_{000} of H_2 dimer.
A . . . electrostatic, B . . . first-order exchange, C . . . dispersion, D . . . induction, E . . . exchange-dispersion, F . . . exchange-induction, G . . . V_{000}.

should take higher-order corrections into account and better basis sets optimizing the interaction energies are required.

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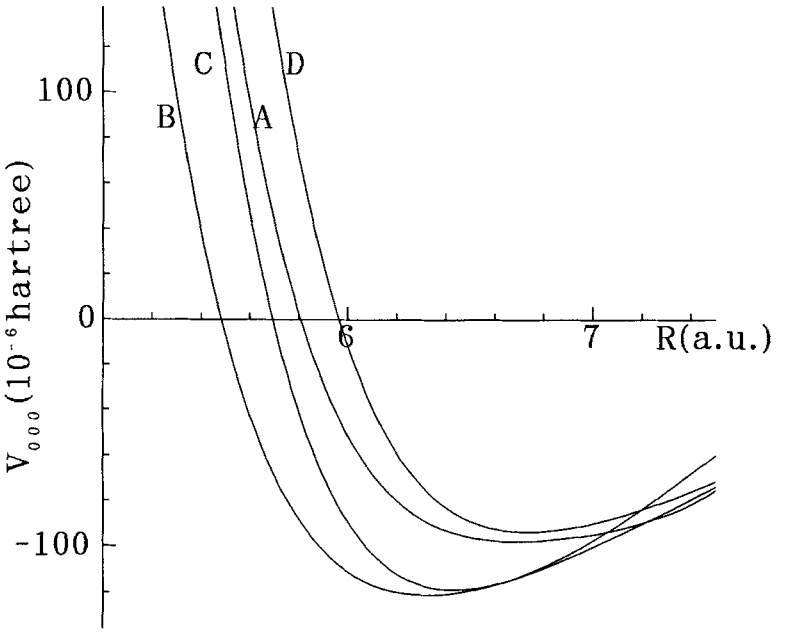

Figure 4 The comparison of the isotropic term V_{000} of our work with those by other authors in H_2 dimer. A . . . ref 2, B . . . ref 5, C . . . ref 7, D . . . our work.

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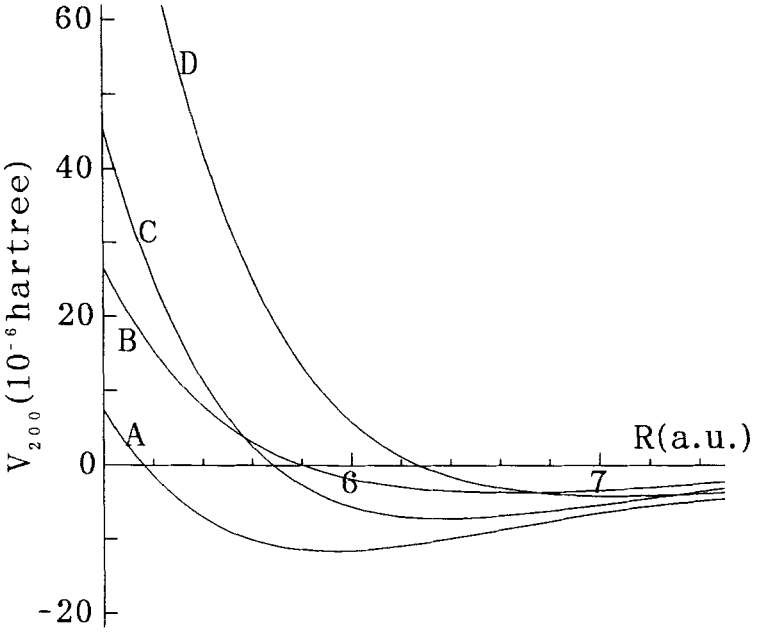

Figure 5 The comparison of the anisotropic term V_{200} of our work with those by other authors in H_2 dimer. A . . . ref 2, B . . . ref 5, C . . . ref 7, D . . . our work.

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