Quantum Mechanical Study of van der Waals Complex.
I. The H₂ Dimer Using the DFT and the Multi-Coefficient G2/G3 Methods

Changsihn Kim, Sang Joon Kim,† Yongsik Lee,* and Yongho Kim*

Department of Chemistry and †Department of Astronomy, Kyung Hee University, Suwon 449-701, Korea
Received April 11, 2000

Molecular hydrogen dimer, $(H_2)_2$ is a weakly bound van der Waals complex. The configuration of two hydrogen molecules and the potential well structure of the dimer have been the subjects of various studies among chemists and astrophysicists. In this study, we used DFT, MCG2, and MCG3 methods to determine the structure and energy of the molecular hydrogen dimer. We compared the results with previously reported *ab initio* method results. The *ab initio* results were also recalculated for comparison. All optimized geometries obtained from the MP2 and DFT methods are T-shaped. The H-H bond lengths for the dimer are almost the same as those of monomer. The center-to-center distance depends on the levels of theory and the size of the basis sets. The bond lengths of the H_2 molecule from the MCG2 and MCG3 methods are shown to be in excellent agreement with the experimental value. The geometry of optimized dimer is T-shaped, and the well depths for the dimerization potential are very small, being 23 cm⁻¹ and 27 cm⁻¹ at the MCG2 and MCG3 levels, respectively. In general the MP2 level of theory predicts stronger van der Waals interaction than the DFT, and agrees better with the MCG2 and MCG3 theories.

Introduction

Molecular hydrogen is a fundamental species in the universe, and it is widely used as a test system in theoretical studies. Molecular hydrogen dimer, $(H_2)_2$ is a weakly bound van der Waals complex. The interaction between two hydrogen molecules attracted many interesting studies especially in the chemistry and astrophysics. In spite of the extensive literature on the spectroscopy of weakly bound molecular complexes, only a few observations of the hydrogen dimer have been reported. The first of these was made in 4100-4500 cm⁻¹ spectra at 20 K by Watanabe and Welsh[1] They suggested that molecular hydrogen dimer may have one vibrational level with a dissociation energy less than 3.5 cm⁻¹. In the spectrum analysis, they used Michels, De Graaff, and Ten Seldam's[2] Lennard-Jones intermolecular potential whose well-depth was estimated to be 25.5 cm⁻¹. After Watanabe and Welsh observed the spectrum, many studies have been done for this system. Gordon and Cashion[3] discussed the spectra in terms of intermolecular potentials. McKellar *et al.*[4,5] concentrated their efforts to get high resolution spectrum of the dimer with possible isotope lines. They explained the weak transition probability as a result of collision induced absorption (CIA) mechanism. According to these results, the molecular hydrogen dimer was found in the spectra of Jupiter as the first detected extraterrestrial dimer.[6,7,8]

The dimerization energy, optimized dimer geometry, and intermolecular potential well depth of the molecular hydrogen dimer have been examined by several different computational techniques. A large number of theoretical and computational investigation on the molecular hydrogen dimer can be found in review articles by Hobza *et al.*[9] and Chalasinski *et al.*[10] A prediction of accurate structure and energy is a critical test for comparison of various computational meth-

ods. The optimized dimer structures were suggested by Tapia and Bessis[11] as one of four possible configurations: linear, parallel, T-shape, and X-orientation. (Figure 1).Using the M ller-Plesset perturbation (MP2) method, Burton and Senff[12] Schneider *et al.*[13] reported that the T-shaped configuration has the lowest energy. Hobza *et al.*[14] calculated the dimerization energy using different basis sets and Möller-Plesset perturbation theory. They concluded that a correction for basis set superposition error (BSSE) should be included at both the SCF and post-SCF levels calculations. Danby and Flower[15,16] calculated the bound state energy levels of molecular hydrogen dimer based upon different intermolecular potential functions. Burton and Senff[7] performed configurational interaction calculations and collision induced band structures. Boothroyd *et al.*[18] obtained *ab initio* energies for mapping the global potential function of H_4 system. Aguado *et al.*[19] got the global potential energy surface at a quantitative level by fitting Boothroyd *et al.* data. Diep and Johnson[20] calculated the potential energy surface with singles, doubles, and perturbational triples excitations for the rigid monomer model.

Examination of the calculated interaction potential can be done by using the differential scattering technique. Farrar and Lee[21] used the crossed molecular beam to study the relatively weak collisional energy encounters of the hydrogen
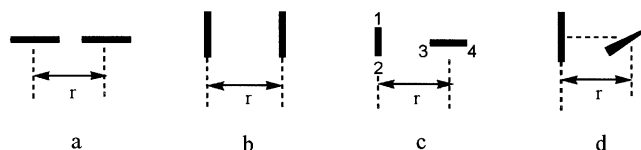
Figure 1. Possible structures of the $H_2\cdots H_2$ dimer. a: linear b: parallel c: T-shape d: X-orientation. Numbers in (c) are hydrogen atom numbers. The same number notation which used in (c) is employed in this study. The center-to-center distances are represented by r in each figures.

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molecules. Buck *et al.*[22] refined the experimental data using the same technique. Their results were in good agreement with the *ab initio* calculations over a range of intermolecular separations of Burton and Senff as well as Schaefer and Koehler.[23]

The calculation of an accurate interaction potential of any van der Waals complex, with the proper geometry optimization, is a theoretical challenge. The accurate calculation of energy and structure is very important because we can extend the employed method to various biological complex system. In that sense, this computational study for molecular hydrogen dimer can be a model testing system for various approaches. The prediction of accurate molecular geometry and energy is usually achieved by the Hartree-Fock (HF) method. In general, the supermolecular approach with proper BSSE corrections gives good result for most dimer systems. However, there are many chemical systems where the implementation of HF calculation fails or just not practical. The major reason is that HF calculations do not address the fundamental issue of electron correlation and the need for a multi reference representation. Inclusion of correlation typically increases the computational costs, thus limiting its application to rather small chemical system.

Today there is increasing evidence that density functional theory (DFT) offers an viable alternative to the HF approach. DFT includes electron correlation in a form that does not lead to the scaling problem of HF based methods. While there is sufficient evidence that DFT provides an accurate description of the electronic and structural properties of solids, interfaces and small molecules, relatively little is known about the systematic performance of DFT applications to molecular dimers. To investigate the applicability of DFT in this field of chemistry, we have performed a systematic DFT study of molecular hydrogen dimers.

The empirical Gaussian-2 method (G2) of Pople *et al.*[24,25] has been successful for computational thermochemistry. There have been many attempts to devise modified G2 methods, typically to decrease the computational cost without a great loss in accuracy. The usual approach was to substitute some of steps or to make changes in the method. Recently, Truhlar *et al.*[26] proposed a modified G2 method, called the multi-coefficient G2 (MCG2) method. For atoms in the Li-Ne period, they showed that MCG2 method improved its accuracy by a factor of 2 with a 10% reduction in computation cost. More recently they have developed the multi-coefficient G3 (MCG3) method[27] and showed that the root mean square error is reduced by about 10% as compared to the G3 method with a reduction in cost of about 50%.

In this study, we used DFT, MCG2, and MCG3 methods to determine the structure and energy of the molecular hydrogen dimer. We compared the results with ones previously reported from *ab initio* methods. Some of the reported *ab initio* results were also recalculated for comparison.

Computational Methods

All electronic structure calculations were performed using Gaussian 94 quantum mechanical package.[28] Geometries for the molecular hydrogen dimer and the hydrogen molecule were optimized at the second order Möller-Plesset perturbation theory (MP2) calculation using 6-311G(d,p), 6-311++G(d,p), and Dunning's correlation consistent double-zeta basis sets[29,30,31] with diffuse functions (aug-cc-pVDZ) in the gas phase.[32] Density functional theory calculations using Becke's[33] three-parameter gradient-corrected exchange functional[34] with the Lee-Yang-Parr[35] gradient corrected correlation (B3LYP) were also performed using the same basis sets. Perdew's[36] nonlocal correlation functional (P86)[37] was also tested. The MCG2 and MCG3 geometries and energies were calculated by using the Multilevel 1.0 program.[38]

The formation energies for the dimer, E_d, were calculated from the difference in energies between the complex and two different monomers. The basis set superposition error (BSSE) may be important in the calculation of the formation energies. The BSSE was corrected by the Boys and Bernardi counterpoise correction scheme[39]

$$\text{BSSE} = [E_m(M_1) - E_d(M'_1)] + [E_m(M_2) - E_d(M'_2)] + E_{reorg} \quad (1)$$

$$E_{reorg} = [E_m(M'_1) - E_m(M_1)] + [E_m(M'_2) - E_m(M_2)] \quad (2)$$

where $E_m(M)$ and $E_d(M')$ are the energies of the monomer in its own basis set and in the basis set of the dimer, respectively, and M and M' denote the optimized geometry of monomer and the geometry of the monomer in the optimized dimer, respectively. The reorganization energy (E_{reorg}) is the deformation energy due to the dimerization. The reorganization energy, the energy associated with the transition from the optimized geometry of monomer to the geometry of the monomer in the dimer, should be also included in the correction of the BSSE. The corrected formation energy is determined as follows:

$$E_d(\text{corr}) = E(D) - [E_m(M_1) + E_m(M_2)] + \text{BSSE} \quad (3)$$

$$= E(D) - [E_d(M'_1) + E_d(M'_2)] + E_{reorg} \quad (4)$$

where $E(D)$ is the energy of dimer.

Results and Discussion

Three kinds of calculations of the molecular hydrogen dimer energy levels were compared. The calculated bond lengths for a hydrogen molecule at the DFT and the MP2 levels of theory using various basis sets are listed in Table 1. When we use the Dunning's correlation consistent double-zeta basis sets, the DFT predicts slightly longer bond length than the MP2 level of theory. In this study, the MP2/aug-cc-pVTZ calculation reproduces the experimental bond length reasonably well. In general the DFT tend to give slightly larger bond length than the MP2 method when the same basis sets were used. The bond lengths from the B3LYP and BLYP methods using the Pople's basis sets also agree very well with experimental results. The DFT calculations with Dunning's augmented double-zeta basis sets don't give very good results, although Dunning's basis sets are much larger

than Pople's.

The BSSE corrected dimerization energies and geometric parameters for the dimer calculated by the DFT and the MP2 level of theory are shown in Table 2. All optimized geometries are T-shaped. The H-H bond lengths for the dimer are almost the same as those of monomer. The center-to-center distance depends very much on the levels of theory and the size of the basis sets. Adding diffuse functions, for example, reduces the distance. This suggests that fairly large basis set is required to obtain correct energy and geometry for the molecular hydrogen dimer. The center-to-center distances at the B3LYP/aug-cc-pVDZ and the MP2/aug-cc-pVTZ levels are 3.4762 Å and 3.4044 Å, respectively. The E_d(corr) values at the MP2 level vary between -0.023 kcal/mol and -0.087 kcal/mol. Our results also meet the single-point full

Table 1. Total energies and bond lengths of H_2 by the MP2 and the DFT methods using various basis sets

Method/Basis Set	Total Energy [hartree]	bond length [Å]
MP2/6-311G**	−1.160272	0.7383
MP2/cc-pVDZ	−1.155222	0.7544
MP2/aug-cc-pVDZ	−1.156216	0.7552
MP2/6-311++G(d.3pd)	−1.164945	0.7361
MP2/aug-cc-pVTZ	−1.165023	0.7374
BLYP/aug-cc-pVDZ	−1.162881	0.7664
BLYP/6-311+-G(d.3pd)	−1.169603	0.7466
B3LYP/cc-pVDZ	−1.173601	0.7617
B3LYP/aug-cc-pVDZ	−1.174024	0.7608
B3LYP/6-311--G(d.3pd)	−1.180029	0.7427
B3P86/aug-cc-pVDZExp	−1.210628	0.7599
Exp		0.7416

Table 2. The BSSE corrected dimerization energies (E_d(corr)) and the geometric parameters for $H_2 \cdots H_2$ by the MP2 and the DFT methods using various basis sets

	Total Energy [hartree]	E_d(corr) [kcal/ mol]	H_1-H_2 [Å]	H_1-H_2 [Å]	Separation Distance^a [Å]
MP2/6-311G**	−2.320595	−0.028	0.7384	0.7384	3.681
MP2/cc-pVDZ	−2.31089	−0.023	0.7544	0.7544	3.6885
MP2/aug-cc-pVDZ	−2.312652	−0.057	0.7548	0.7549	3.3171
MP2/6-311+-G(d.3pd)	−2.330017	−0.055	0.7367	0.7367	3.4688
MP2/aug-cc-pVTZ	−2.330201	−0.087	0.7376	0.7376	3.4044
BLYP/aug-cc-pVDZ	−2.325665	−0.004	0.7661	0.7661	3.4845
BLYP/6-311+-G(d.3pd)	−2.339128	0.062	0.7472	0.7473	4.0869
B3LYP/cc-pVDZ	−2.347177	−0.014	0.7617	0.7617	3.4850
MP2/6-311G**	−2.348040	−0.041	0.7607	0.7607	3.4762
MP2/6-311G**	−2.359967	0.066	0.7427	0.7427	3.4411
MP2/6-311G**	−2.421122	−0.023	0.7598	0.7498	3.4905

^{a}The distance between the centers of two hydrogen monomers.

configuration interaction (FCI) calculation results from Diep and Johnson.[20] They suggested that the BSSE corrected binding potetial energy be -38.050 K, or -26.43 cm^{-1}, at the center-to-center distance of 3.4 Å. When we use larger basis sets, the E_d(corr) values become more negative,*i.e.*, the van der Waals interaction becomes stronger. We have observed the same trend for the DFT level when we used Dunning's basis sets. However, BLYP method reports unacceptable large separation distance at 6-311++G(d, 3pd) basis set level. The B3LYP and BLYP methods using Pople's 6-311++G(d, 3pd) basis set give positive E_d(corr) values, which are not physically correct, either. Although they reproduce the bond length of H_2 molecule very well, as shown in Table 1, their dimerization energies are not very reliable. When we used the same basis sets, the MP2 level of theory predicts stronger van der Waals interaction than the DFT.

Considering the weak intermolecular interaction, calculated harmonic vibrational frequencies for the H-H stretching in the dimer can be compared with the experimental harmonic vibrational frequencies of a hydrogen molecule. Calculated vibrational frequencies are shown in Table 3 where no imaginary values were found. And the scaling procedures were not employed for clearer comparision between the computational methods. Since the full IR spectrum of the dimer is not available yet, molecular hydrogen monomer vibrational frequencies, which is 4395 cm^{-1}, is the only experimental values we can compare with. As in the hydrogen molecule monomer case, MP2 methods produce slightly larger vibrational frequencies for the H-H stretching modes than the B3LYP methods.

The optimized geometries and energies for the molecular hydrogen and the dimer using the MCG2 and MCG3 methods were shown in Table 4. The bond lengths of the hydrogen molecule from the MCG2 and MCG3 methods are 0.7424 Å and 0.7417 Å, respectively, and they agree very well with experiment.[40] In particular, the calculated bond length using the MCG3 method is almost identical to the experimental value. The H-H bond length becomes slightly longer due to the formation of the dimer. The optimized

Table 3. Vibrational frequencies of $H_2 \cdots H_2$ by the MP2 and DFT methods using various basis sets

	Frequencies [cm^{-1}]					
	A1	B2	B1	B2	A1	A1
MP2/6-311G**	36	48	66	80	4532	4533
MP2/cc-pVDZ	30	47	68	81	4501	4501
MP2/aug-cc-pVDZ	80	94	126	132	4460	4463
MP2/6-311+-G(d.3pd)	49	67	84	118	4515	4516
MP2/aug-cc-pVTZ	62	76	102	126	4514	4516
BLYP/aug-cc-pVDZ	50	85	110	111	4367	4270
BLYP/6-311+-G(d.3pd)	20	131	136	145	4327	4328
B3LYP/cc-pVDZ	48	68	84	114	4367	4368
B3LYP/aug-cc-pVDZ	44	75	102	112	4353	4356
B3LYP/6-311-+G(d.3pd)	22	66	80	109	4410	4411
B3P86/aug-cc-pVDZ	38	68	94	114	4366	4370

Table 4. Energies and geometries of $H_2 \cdots H_2$ by the MCG2 and MCG3 calculations

	MCG2(SP)[a]	MCG2[b]	MCG3[c]	Exp.[d]
	Monomer			
R(H-H)	0.7376 Å	0.7424 Å	0.7417 Å	0.7416 Å
Energy[e]	−1.165058	−1.165184	−1.169323	
	Dimer			
R(H1-H2)	0.7376 Å	0.7425 Å	0.7419 Å	
R(H3-H4)	0.7376 Å	0.7425 Å	0.7419 Å	
Center-to-Center Distance	3.4044 Å	3.4467 Å	3.4247 Å	
Energy[e]	−2.330151	−2.330473	−2.338768	
Dimerization Energy[f]	−0.019	−0.066	−0.076	

[a]Single point calculations using the geometries optimized at the MP2/aug-cc-pVTZ level. [b]For the basis sets, see reference 26. [c]For the basis sets, see reference 27. [d]From the hydrogen molecule monomer data. Herzberg, G., *Molecular Spectra and Molecular Structure I*; VNR: New York, 1950; p 532. [e]In hartree. [f]In kcal/mol.

geometry for the dimer is again T-shaped, and the center-to-center distances from the MCG3 and MCG2 methods are 3.4247 Å and 3.4467 Å, respectively. There is no precise experimental data for this distance. We believe that these are one of the highest level calculations for the optimized structure of the molecular hydrogen dimer so far, therefore the experimental value would not be much different from these values. The corrected dimerization energies were also calculated, which are -0.07 kcal/mol and -0.08 kcal/mol at the MCG2 and MCG3 levels, respectively. They are equivalent to 23 cm⁻¹ and 27 cm⁻¹ of well-depths, respectively. These well-depths agree very well with experiment.[1,21] Comparing with the results from the MCG2 and MCG3 methods, the bond lengths and the dimerization energies from the MP2 level of theory agree better than those from the DFT methods. The DFT methods with Dunning's basis sets, which seem to be more reliable than that with Pople's basis sets especially for this system, tend to underestimate the well-depth and overestimate the center-to-center distance of the dimer and the H-H bond length.

Conclusion

The dimer of hydrogen molecule, $(H_2)_2$, is an astronomically important species and a theoretically well-studied four atom system. Although the dimer has been extensively studied, this weakly bound molecule remains as a theoretical and experimental challenge. We have fully optimized the configuration of the molecular hydrogen dimer at the MP2, B3LYP, and the BLYP levels of theory using various basis sets. The MP2 methods predict frequencies higher than the experimental value. And the BLYP, B3LYP, B3P86 methods have longer bond lengths. The newly proposed MCG2MCG3 methods were also used to calculate geometries and energies. The bond lengths of the H_2 molecule from the MCG2/MCG3 methods agree extremely well with the experimental value. The geometry of optimized dimer is T-shaped, and

the well depths for the dimerization potential are very small, which are 23 cm⁻¹ and 27 cm⁻¹ at the MCG2 and MCG3 levels, respectively. In general, the MP2 level of theory predicts stronger van der Waals interaction than the DFT method, and agrees better with the MCG2 and MCG3 methods.

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